Great Smoky Mountains National Park 2012 Water Quality Annual Report

Natural Resource Data Series NPS/GRSM/NRDS—2013/XXX

Middle Prong Little River

Great Smoky Mountains National Park 2012 Water Quality Annual Report

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Abstract/Executive Summary

The GRSM annual Water Quality (WQ) Monitoring Program consists of: 1) detailed hydrologic and WQ monitoring at Noland Divide, a high-elevation forested site; and 2) Park-wide stream survey during baseflow conditions and 3) a summary of the data collected on the impacts of a concrete truck rollover into Watercress Branch and subsequent monitoring. This report gives a summary and brief analysis of all data collected for the GRSM monitoring program, including historic data since 1993 and the most recent 2012 results. At the Noland Divide site, the annual mean pH for the throughfall (TF) was 5.16; pH at this location continues trending up from the low mean pH of 3.91 reported in 1991. Since 2008, sulfate mass deposition in TF remains low at 687 eq/ha/yr compared with prior historic levels (>1,500 eq/ha/yr). Reduction in sulfate deposition likely is the result of coal-fired power plant closures and pollution control facilities installed at near-by Tennessee Valley Authority plants at Bull Run and Kingston. Total inorganic nitrogen (TIN) in TF continued to increase from a low of about 610 eq/ha/yr in 2010 to 1,153 eq/ha/yr in 2012. The 2012 increase in TIN is particularly due to elevated concentrations of ammonium, which has also been observed nationally by NADP and attributed to vehicle exhaust and agricultural sources. Elevated levels of deposited ammonia nitrogen can cause stream acidification when converted to nitrate by soil mineralization and nitrification. Among the Park-wide stream survey sites, 20 of 186 samples collected had a value below a pH of 6.0. Ten samples had a pH less than 5.5, which is a toxic threshold impairing trout growth; and dissolved aluminum concentrations for 14 samples were recorded at 0.2 mg/L, a known toxic threshold for that metal. These data indicate that aluminum is being leached from soils and transported to streams. Collectively, the mean pH of streams in the Park-wide survey in 2012 was 6.50, a slight improvement over the average pH of 6.44 from 1993 – 2011. Data from both 2012 monitoring programs data suggests a shift from sulfate controls on stream acidity in previous years, to controls governed by nitrogen deposition and base cation export. Additional monitoring and analysis is needed to verify this preliminary observation with current water quality trends. This report summarized water chemistry by individual drainage basin, and even individual sampling site; where differences were found based on site elevation and local geology. Finally, water chemistry data for the special water quality monitoring project on Watercress Branch related to a concrete spill in that small stream indicates that the stream has recovered completely.

Acknowledgments

List of Terms, Small Glossary, Acronyms, or Contacts

ANC	Acid Neutralizing Capacity
BDL	Below Instrument Detection Limit
CEE	Department of Civil and Environmental Engineering
CV	Coefficient of Variation
DI	Deionized Water
eq/ha/yr	Equivalents per hectare per year
GRSM	Great Smoky Mountain National Park
IC	ion chromatograph or ion chromatography
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectrometry
N	Nitrogen
NADP	National Atmospheric Deposition Program
NDW	Noland Divide Watershed
NPSTORET	National Park Storage and Retrieval
OS	Open Site
QA/QC	Quality Assurance / Quality Control
QCC	Quality Control Check
T.I.N.	Total Inorganic Nitrogen
TF	Throughfall
UTK	University of Tennessee - Knoxville
WQ	Water Quality

1.0 Introduction

Since the 1980's national air quality monitoring has shown that the Great Smoky Mountain National Park (GRSM) receives high rates of atmospheric deposition of acid pollutants compared to other regions in the United States (Shubzda et al. 1995; NADP 2009; Sullivan et al. 2007; Silsbee and Larson 1982; Barnett 2003; Harwell 2001). These pollutants have been linked to emissions from regional coal-fired power plants (Chestnut and Mills 2005; Stachurski and Zimka 2002; Stoddard 1994; Weathers et al. 2006). In the eastern United States, high elevation watersheds with base-poor cation buffering capacity tend to be vulnerable to stream acidification from acid deposition (Hyer et al. 1995; Driscoll et al. 2001). Most of the GRSM streams are low in acid neutralizing capacity (ANC), and exhibit acidification (lowered pH) chronically and episodically (Robinson et al. 2008; Deyton et al. 2008). A major concern of stream acidification in watersheds that lack acid buffering capacity is the transfer of potentially toxic aluminum from soil to streams (Cai et al. 2011a, 2012; Baldigo and Murdoch 1997; Neff et al. 2009). Initial investigations into the potential impacts to water quality from atmospheric deposition of acid pollutants began in the 1970's but were sporadic. In the early 1990s, GRSM initiated a long-term water quality (WQ) monitoring program.

The current WQ program consists of two primary components: 1) detailed hydrologic and WQ monitoring at Noland Divide, a high-elevation forested site; and 2) Park-wide stream survey primarily characterizing baseflow WQ conditions. In addition for 2012, a special study was conducted on behalf of GRSM management to address a specific management issue pertaining to Watercress Branch.

2.0 Noland Divide Watershed

Noland Divide watershed (NDW) was selected as a part of the long-term water quality-monitoring program in 1991 after completion of the Integrated Forest Study. The Integrated Forest Study was an American and European program to study acid rain effects on forest nutrient cycling, in which Noland Divide was one of several sites studied (Johnson and Lindberg 1992; Lindberg and Lovett 1992). Ongoing monitoring at NDW continues to provide data used to understand potential effects associated with acidic deposition, and to generate data for estimating critical loads at high elevation areas in the GRSM through the use of the Pn-ET BGC Model (Zhou et al. 2011).

2.1 Introduction

NDW is located in the GRSM about a half-mile from Clingman's Dome on the border of North Carolina and Tennessee at 35º 34' N latitude and 83º 29' W longitude. NDW is a small, 17.4 ha forested watershed ranging in elevation from 1,680 m to 1,920 m (Figure 1). Two adjacent first-order streams originate from this watershed (NE and SW streamlets) and merge to form Noland Creek. The mean annual air temperature measured at a climate station, located about 100 m below the watershed outlet, is approximately 8.5°C, ranging from -2°C in January to +18°C in July, with a frost-free period from May through September (Shanks 1954; Van Miegroet et al. 2001). The annual precipitation ranges from 200 cm to 300 cm, 10% of which is accounted by snow (Johnson et al. 1991; Johnson and Lindberg 1992). NDW's vegetative overstory consists of old-growth red spruce, and interspersed patches of dead Fraser fir (Nodvin et al. 1995).

Soils in the NDW are inceptisols with spodic characteristic, classified as Dystrochrepts or Haplumbrepts (McCracken et al. 1962; Van Miegroet et al. 1993). They have a silt loam to sandy loam texture, and are generally shallow throughout the NDW. Johnson and Lindberg (1992)

characterized the NDW soil as consisting of a 4 cm thick Oi + Oe horizon of needles and leaves, a 4-cm thick Oa horizon of organic humus, an 8 cm thick A horizon of dark, reddish-brown, mucky loam, a 27-cm thick Bw horizon of dark brown, sandy loam, a 35 cm thick Cb horizon of dark, yellowish-brown loam, a 20+ cm thick C horizon of olive-brown, loamy sand, and underlying sandstone bedrock. Underneath the soil is massive thick-bedded and low porosity Thunderhead sandstone, composed of quartz and potassic feldspar (King et al. 1968).

2.2 Study Activities and Methods

Five NDW hydrological stations were installed to monitor the potential effects of long-term acid deposition (Figure 1). These stations include: wet precipitation (open site, OS), throughfall (TF), soil water from lysimeters, and two streamlets (southeast, SE, and northeast, NE sites). This monitoring design provides a means to assess impacts from acidic deposition, both wet and dry deposition (OS, TF sites), effects of soil biogeochemical processes on pollutant fate and transport, and stream acidification responses based on levels of atmospheric acid inputs to the watershed (Jin et al. 2006).
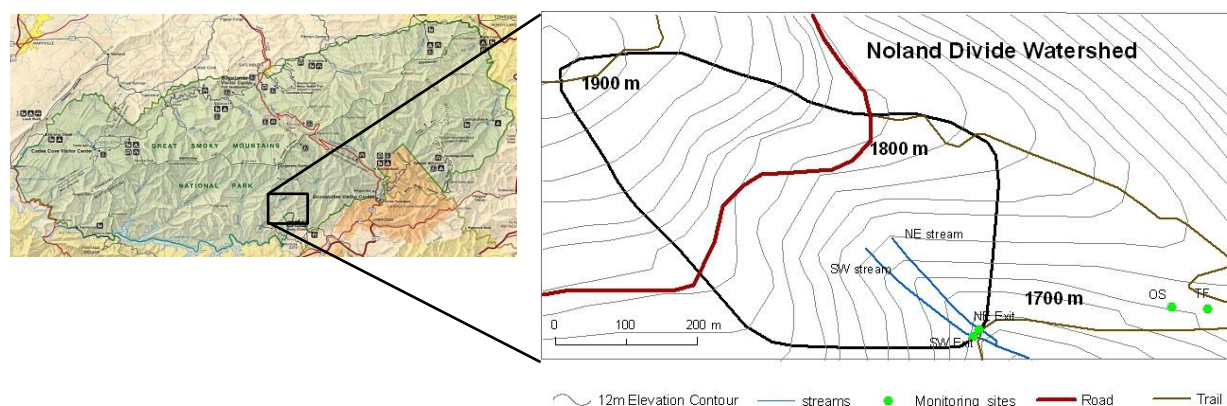
Figure 1. Map of Noland Divide watershed showing water quality monitoring stations (OS = open site, TF = throughfall site, SW and NE = streamlet sites).

Every two weeks wet and throughfall precipitation (OS, TF) samples are collected at sites located on the NE side of the watershed. Wet-only precipitation is collected at the OS station, where there is no tree cover and it is fully exposed to atmosphere. TF collection is deployed under the canopy at the same elevation approximately 50 m east of the OS station. Collected water samples from OS and TF stations are weighed in order to compute volumes, and brought back to University of Tennessee – Knoxville (UTK) Department of Civil and Environmental Engineering (CEE) laboratory for chemistry analyses (Appendix A).

Stream water quality and discharge are measured at the watershed outlet for the SW and NE streams. Stream flows are estimated by use of H-flume weirs and GlobalWater® WL16 stage recorders installed at each stream. Stage recorders measure flow depth every 15 minutes, and discharge is computed by H-flume standard formulas from the depth measurements. Water quality is continuously monitored with YSI600R® or Eureka Manta I sondes (pH, conductivity and temperature). The SW sonde data collection began in July 1991 and the NE sonde began in April 1998. Data sondes record data every 15 minutes. Grab samples of stream water are collected from the NE and SW streams every two weeks and brought to the UTK-CEE lab for chemical analyses.

Soil water is collected by ceramic suction lysimeters originally installed in 1991 with four per each of three different soil horizons (A, B_w, and C_b horizons). Soil lysimeters are located adjacent to the

TF precipitation station (Figure 1). Soil water was collected on a biweekly or monthly basis dependent on the amount of rainfall and volume in the collection bottles. Collection bottles must contain 100 ml in order to have sufficient volume for chemical analysis. During the past two years lysimeter probes began to fail due to 20+ year age. A major maintenance effort of the suction tubing and bottles was completed in 2012. Although 2 A horizon, 1 B_w horizon and 1 C_b probes have failed, soil water samples were collected among all three horizons with the remaining functional lysimeters. New lysimeters at all three horizons will be installed in 2013.

The Noland Divide Watershed (NDW) sample set for 2012 consists of 132 samples, divided as follows: 20 samples from OS, 21 samples from TF, 21 samples each from the northeast (NE) and southwest (SW) branch of the stream, and 49 from soil lysimeter sampling. The following sections summarize the data obtained from these samples in 2012, and the comparison between them and historical NDW data collected since 1991 (through end of 2011).

2.3 Annual Precipitation Volume
The annual rainfall volumes collected during 2012 were 211.1 cm at the TF and 196.7 cm at the OS (Figure 2). By visual inspection, these volumes were similar to past three years.
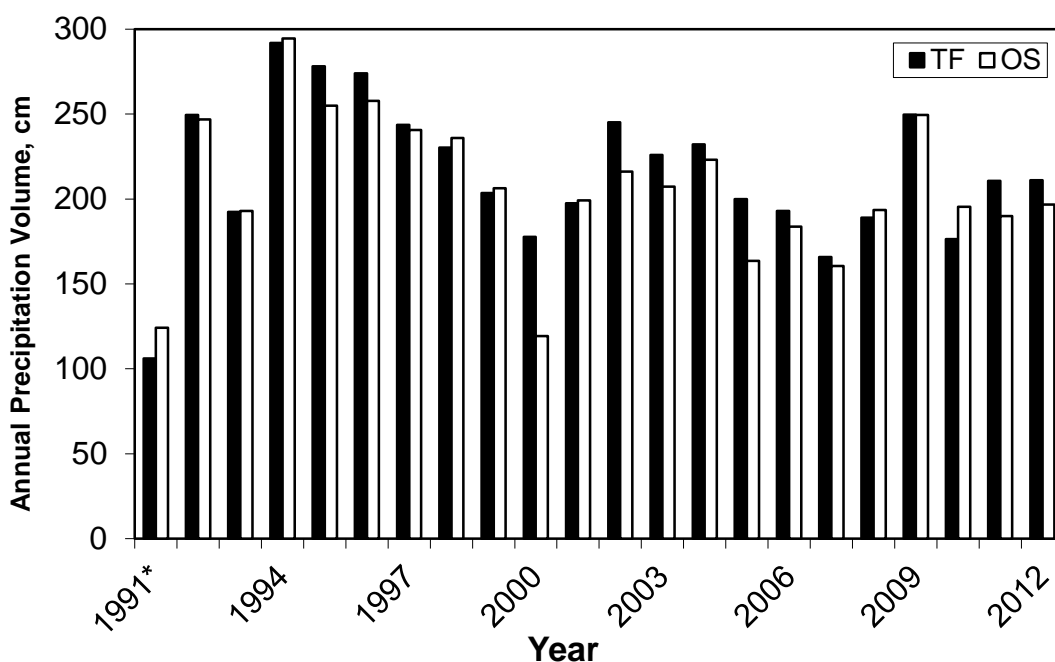
Figure 2. Total annual precipitation volumes at throughfall (TF) and open site (OS) in the NDW. *Sampling in 1991 began mid-year; that year's data do not represent the entire year.

2.4 Annual Deposition Rates for Chemical Constituents
Annual rates of deposition (per unit watershed area) of chemical constituents are summarized for TF and OS precipitation, and compiled in the National Park "Storage and Retrieval" (NPSTORET) database for the GRSM. This annual report presents data only for nitrogen and sulfur constituents because of their dominant influence on stream acidification. Concentration data for other anions/ cations and dissolved metals can be found in NPSTORET.

In 2012, average throughfall pH collected at the TF site was 5.16, and this measurement was the second highest pH for the period of record. Throughfall pH at this site has increased gradually from

a low of 3.98 in 1991 to its current level. Similarly, the average precipitation pH at the OS was 5.28, lower than the annual average of the previous four years, but was higher than the average pH of 4.88 at this site for the period of record. The OS pH also has increased from 4.35 in 1991. This trend in part reflects decreases in atmospheric sulfate and nitrogen inputs.

During 2012, the total sulfate mass flux entering the NDW via throughfall was estimated to be 687.0 equivalents of sulfate (SO_4^{2-}) per hectare per year (eq/ha/yr), and OS precipitation was 247 eq/ha/yr (Figure 3). At the TF site, the sulfate flux deposited in 2012 was the second lowest amount estimated during the period of record. At the OS, annual sulfate deposition has generally remained within the 300 to 700 eq/ha/yr range. Decreasing trends are believed to be related to lower atmospheric pollutant inputs to the GRSM, a direct result of lower emissions from regional coal-fired power plants. However, deposition measurements are highly dependent on rainfall volumes; i.e., OS mass flux during drought years will be less than during wet years. Correlations between pollutant deposition and power plant emissions are presented in Section 2.7.
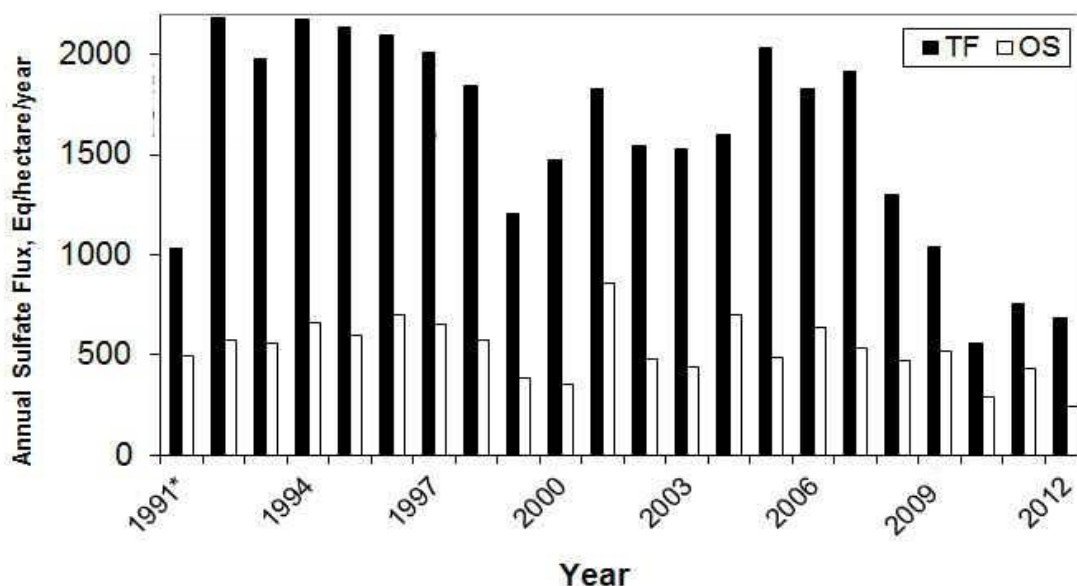
Figure 3. Total sulfate entering NDW via precipitation measured at TF and wet-only OS. *Sampling in 1991 began mid-year; those data do not represent the entire year.

During 2012, total inorganic nitrogen (T.I.N.) mass entering the NDW via throughfall was estimated to be 1,153 N eq/ha/yr and OS precipitation was 392 N eq/ha/yr (Figure 4). At the TF site, the T.I.N. load deposited in 2012 was slightly higher than the previous year. Conversely by visual inspection, the T.I.N. load deposited at OS was near the mid-range over the period of record. Ammonium represented ~31% and ~33% of T.I.N. inputs to TF and OS, respectively, in 2012.

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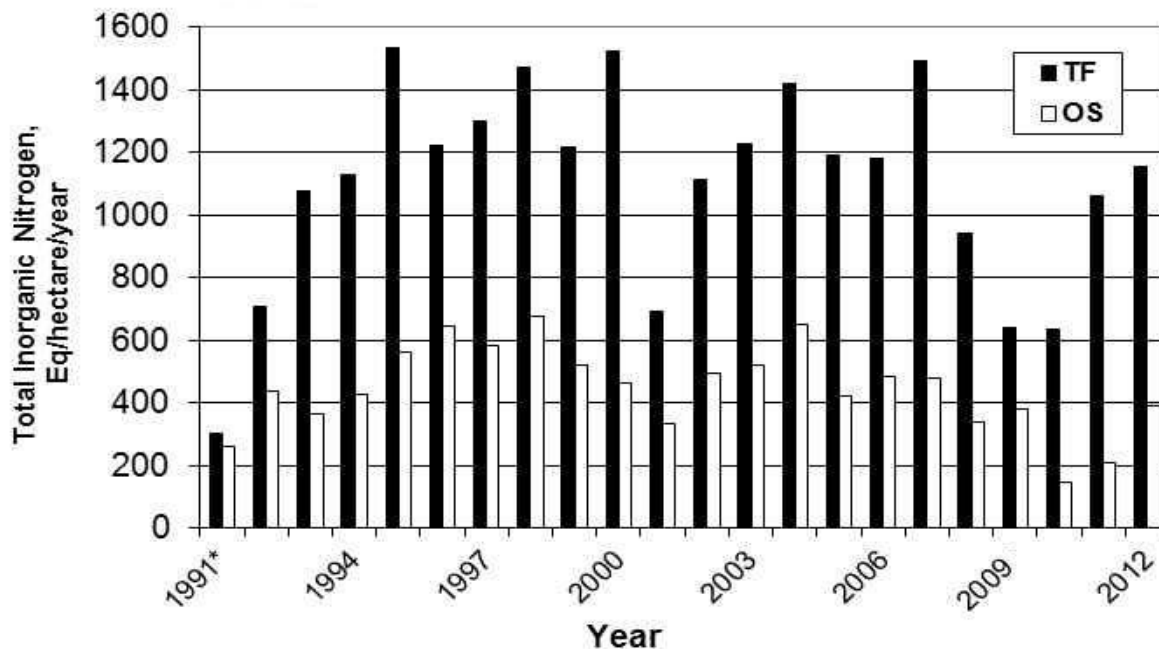
Figure 4. Annual total inorganic nitrogen (TIN) deposited in the NDW via precipitation at TF and OS. *Sampling in 1991 began mid-year; that year's data do not represent the entire year.

Another trend noted is the changing nitrogen chemistry over time in water from the TF site. T.I.N. in this study is the sum of nitrate and ammonium concentrations. In Figure 5, the percentage of T.I.N. represented by ammonium is plotted with the corresponding T.I.N. values over the period of record. There appears to be a systematic relationship between the ammonium *fraction* of T.I.N. and water pH at the TF site. As stream water pH increases, the ratio of nitrate-to-ammonium in T.I.N. decreases. The same relationship was not clearly observed in the OS site data (not shown). Although interesting, more investigation is needed to confirm this relationship and to develop a plausible explanation.
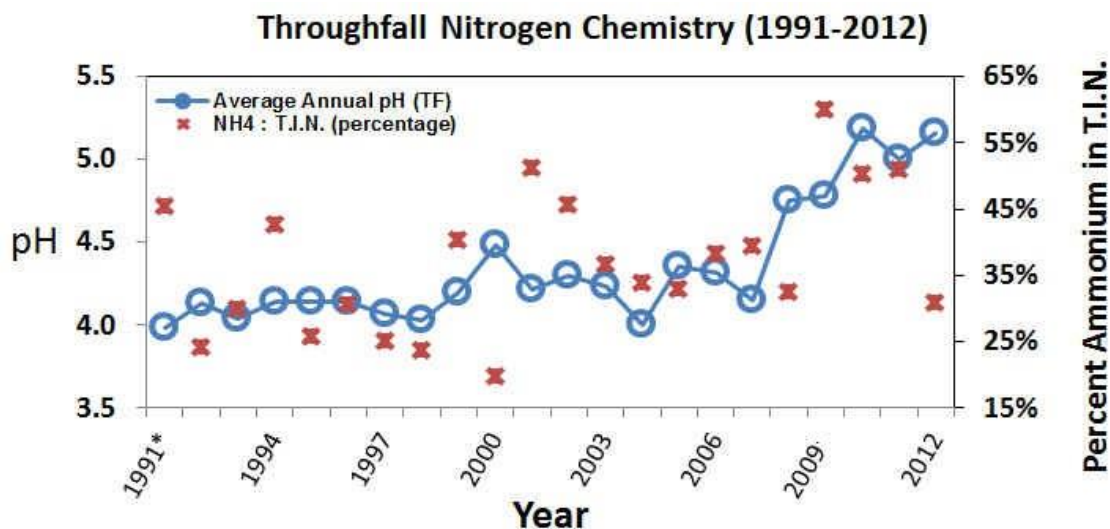
Figure 5. Percentage of ammonium in T.I.N. at the throughfall (TF) site, and the corresponding pH of site water per year. Left axis is pH; right axis is percent ammonium in T.I.N. *Sampling in 1991 began mid-year; that year's data do not represent the entire year.

2.5 Soil Water Chemistry from Lysimeters

Soil water samples were collected monthly from 8 of the 12 lysimeters (4 located at 3 different depths; upper A horizon 8 cm; middle B_w horizon 35 cm; and lower C_b horizon 65 cm). The annual volumes of water from the upper, middle, and lower lysimeters were 1,376 milliliters (mL), 6,666 mL, and 5,990 mL, respectively.

The soil water pH for 2012 averaged 3.91 for the upper A horizon, 4.30 for the middle B_w horizon, and 4.68 for the lower C_b horizon (Table 1). The trend from lower pH at the upper A horizon to a higher pH at the lowest C_b horizon was primarily due to the higher nitrate in the A horizon and the higher base cations in the C_b horizon (Tables 2 and 3). Comparing the 2012 averages for soil water pH to the 1991-2011 long-term averages, pH decreased 0.14 units in the A horizon, decreased 0.07 units in the B_w horizon, and increased by 0.20 units in the C_b horizon.

Except for chloride in the middle horizon, anion concentrations in 2012 were lower than previous years' averages (Table 2). Chloride in the upper (A) and lower (C_b) soil horizons decreased 9.97 µeq/L and 6.88 µeq/L, respectively. Sulfate in the upper (A), middle (B_w), and lower (C_b) horizons decreased 27.63 µeq/L, 33.52 µeq/L, and 24.32 µeq/L, respectively.

Table 1. Statistical summaries for pH and conductivity from the soil lysimeters.

		pH	Conductivity, µS/cm^2
Upper Lysimeter	2012 Average	3.91	68.32
	1991-2011 Min- Max	**3.36-5.18**	**1.31-179.10**
	1991-2011 Average	4.05	63.57
Middle Lysimeter	2012 Average	4.30	37.38
	1991-2011 Min- Max	**3.55 – 5.85**	**11.53 – 152.90**
	1991-2011 Average	4.37	39.66
Lower Lysimeter	2012 Average	4.68	25.49
	1991-2011 Min- Max	**3.79 – 5.37**	**14.31 – 102.90**
	1991-2011 Average	4.48	33.66

Table 2. Statistical summaries of the anion chemistry analysis from the soil lysimeters.

Values in micro-equivalents per liter (µeq/L)		Cl$^-$	NO$_3^-$	SO$_4^{2-}$
Upper Lysimeter	2012 Average	17.68	98.65	62.52
	1991-2011 Min- Max	**1.61-229.53**	**0-784.94**	**0-316.93**
	1991-2011 Average	27.65	137.40	90.15
Middle Lysimeter	2012 Average	31.16	52.13	64.99
	1991-2011 Min- Max	**5.04 – 228.35**	**0 – 478.50**	**44.86 – 334.49**
	1991-2011 Average	26.56	74.80	98.51
Lower Lysimeter	2012 Average	16.40	57.51	66.03
	1991-2011 Min- Max	**0 – 238.21**	**4.20 – 270.42**	**28.67 – 170.12**
	1991-2011 Average	23.28	83.14	90.35

Table 3. Statistical summaries of the cation chemistry analysis on the soil lysimeters.

Values in micro-equivalents per liter (µeq/L)		Na⁺	K⁺	Mg²⁺	Ca²⁺
Upper Lysimeter	2012 Average	28.68	8.79	14.67	22.27
	1991-2011 Min- Max	**0 - 482.62**	**0 - 103.73**	**2.12 – 249.38**	**0 – 577.50**
	1991-2011 Average	26.20	22.16	27.04	54.88
Middle Lysimeter	2012 Average	33.75	12.15	17.24	24.98
	1991-2011 Min- Max	**2.81 – 84.03**	**0 – 168.00**	**0 – 38.60**	**0 – 128.10**
	1991-2011 Average	23.14	9.61	20.51	28.09.
Lower Lysimeter	2012 Average	22.56	7.42	23.71	48.9
	1991-2011 Min- Max	**0 – 57.23**	**0 – 109.31**	**8.62 – 43.76**	**6.30 – 216.50**
	1991-2011 Average	19.72	9.36	23.88	37.10

Nitrate in the upper (A), middle (B_w), and lower (C_b) horizons increased 2.48 µeq/L, 10.61 µeq/L, and 2.84 µeq/L,respectively. The average base cation chemistry in 2012 was similar to the average for all previous years (Table 3). Temporally, the lower soil pH in A and B_w horizons and higher pH in the C_b horizon is partially explained by the measured increase in soil calcium concentration in C_b soil horizon and the decrease in soil calcium in the B_w horizon.

2.6 Stream Water Chemistry

Stream water quality samples were collected from the SW and NE streamlets biweekly. Results of chemical analysis of those samples are presented in Figure 6. Plotted (left to right) are 2012 data and combined pre-2012 data for general water chemistry parameters (conductivity, pH and ANC), major anions (chloride, nitrate and sulfate), ammonium and base metals (sodium, potassium, magnesium and calcium), and aluminum.

In general, annual average values of most water chemistry parameters for 2012 are similar to overall average values for pre-2012 data. Annual average ammonium concentrations in both TF and OS show a marked increase in 2012 relative to all prior monitoring years. This observation might be related to the increased T.I.N. deposition in TF and OS measured in 2012 (Figure 4). Also, annual average ANC concentrations in both TF and OS show a marked increase in 2012 relative to prior years. This is consistent with the relative increase in stream pH being observed at Noland Divide.

2.7 Noland Divide Data Comparisons with TVA Power Plant Emissions

Acid-forming pollutants are transported to the GRSM by prevailing wind currents arriving from several air-borne pollutant sources. Examples include two Tennessee Valley Authority (TVA) fossil fuel power plants (Bull Run and Kingston) located within 100 miles of GRSM. TVA has initiated pollutant reduction measures over the years, including operational changes in the 2003-2004 and air pollution controls in 2008-2009 (TVA 2013). Data from the NDW monitoring program was used to identify responses in the GRSM water chemistry due to reductions in sulfate and T.I.N. resulting from TVA's air emission abatement activities. The two plots in Figure 7 show a number of parameters over the period of record (1991 – 2012).   The top panel shows annual average concentrations of sulfate in the four sampling locations (OS, TF, SW and NE) against published annual emission data for mass of sulfur dioxide (in units of 1000 tons). The bottom panel presents the same set of data for T.I.N. (sum of measured nitrate and ammonium).

The largest changes in measured ions were associated with mean annual throughfall concentration. For both sulfate and T.I.N., concentrations peak in 2007 and drop precipitously in the next two to three years. Sulfur and T.I.N. concentrations at TF site are influenced by emissions release from other power plants and vehicles, thus many other actors affect the correlation between water chemistry and the two TVA power plants. However, it is interesting the temporal correlated shifts in variables. Noland Divide throughfall T.I.N. (on an annual basis) exhibits a wider range of variability than sulfate concentrations at all NDW sites. Also, stream sulfate concentrations did not show a decline over time, whereas T.I.N has shown a slight decline. Stream chemistry is dependent of soil biogeochemical processes, and it appears sulfate continues to be absorbed by the soil regulating sulfate transport from throughfall to stream.
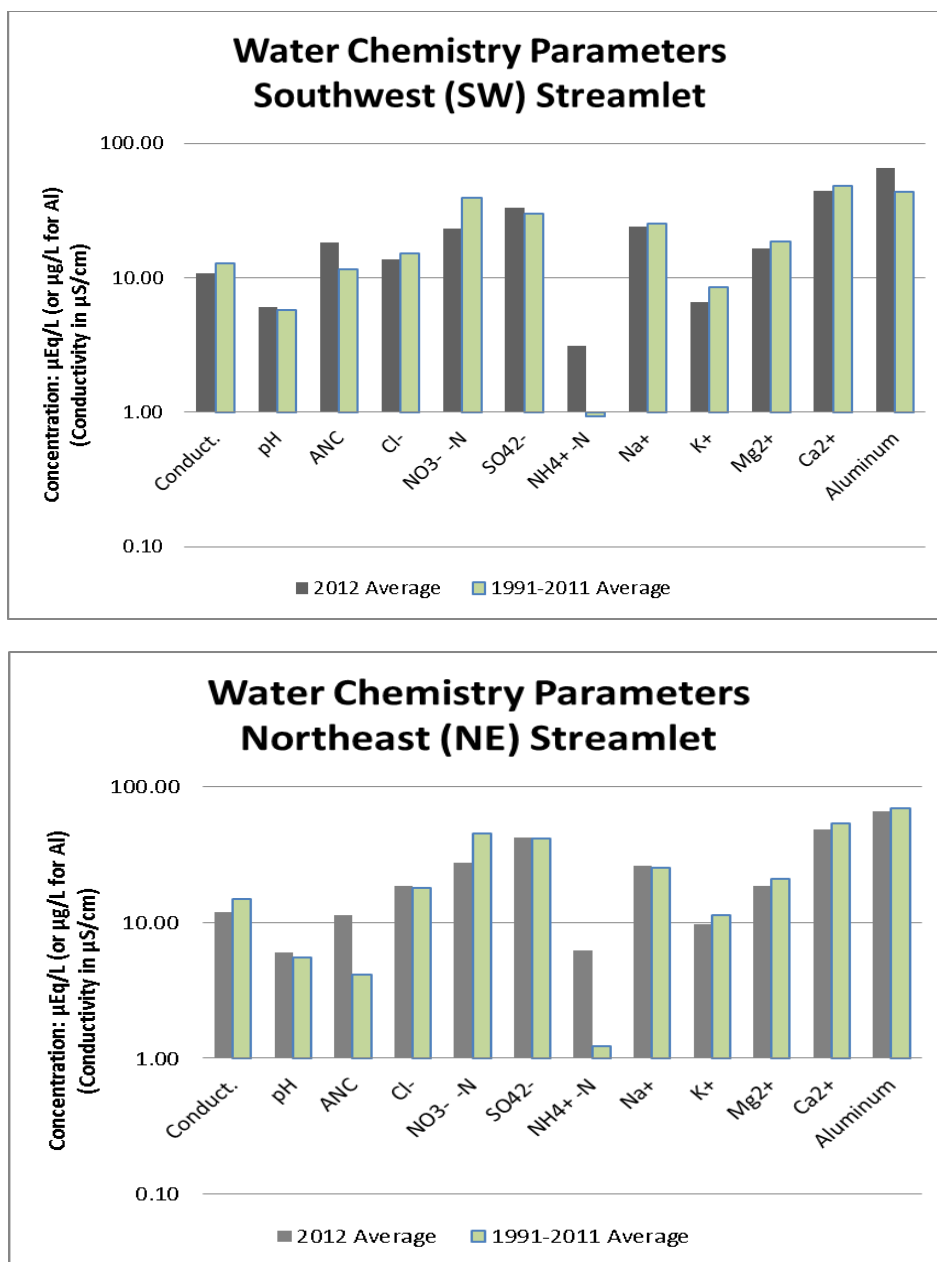
Figure 6. Summary of water chemistry in the SW and NE streamlets of the Noland Divide study site. All parameter values are given in μeq/L, except for pH given as pH units, conductivity in μS/cm, and Al in mg/L.
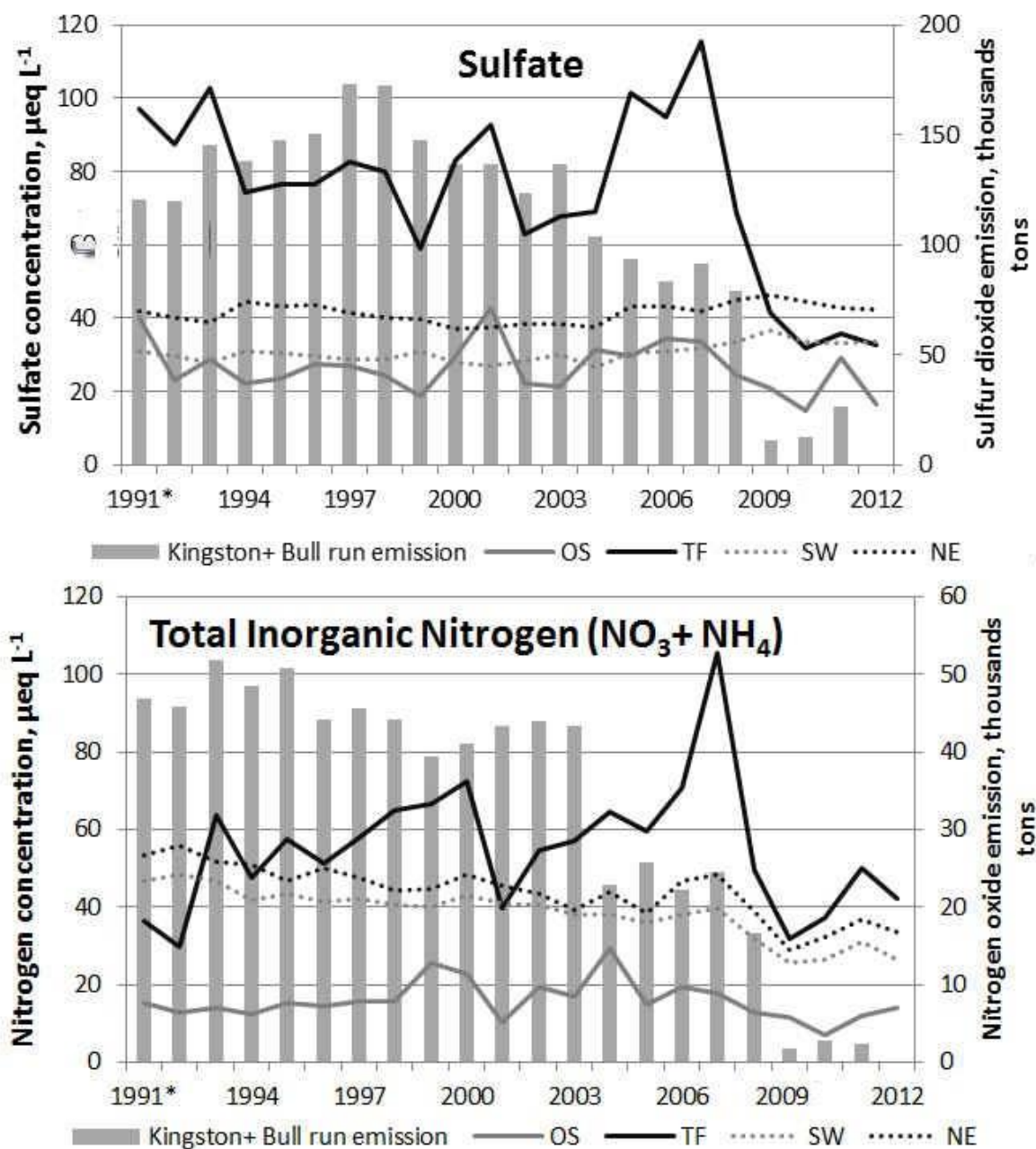
Figure 7. Sulfate and nitrogen concentrations in annual volume-weighted concentrations in deposition and streams, and total emissions from Bull Run and Kingston Power Plants. *Sampling in 1991 began mid-year; that year's data do not represent the entire year.

3.0 Park-wide Stream Survey

3.1 Introduction

Park-wide stream survey (also termed long-term synoptic stream WQ monitoring) began in October 1993 to monitor water quality in GRSM streams, and simultaneously to assess possible correlations between GRSM water chemistry and atmospheric sources of acid-generating pollutants. The total number of sampling sites included in the monitoring program has been reduced from the original 367 (1993 to 1995) collected semi-annually, to the current 43 sites since 2003 (Schwartz et al. 2013). The current sites (Figure 8) are distributed among seven watershed drainage basins identified by their predominant surface water body: Abrams Creek (4 sites); Cataloochee Creek (8 sites); Cosby Creek (4); Little River (3); Oconaluftee River (5); Road Prong/Rt.6 (8); and Hazel Creek (11). These drainage basins were selected to best represent the natural spatial variability in elevation, geology types, and land use/ disturbance histories found in the GRSM (Odom 2003). Location information for these sites is given in Appendix B.

Since program inception in 1993, a valuable database of water quality parameters has been developed, which has been recently analyzed in a GRSM report on water quality effects on aquatic biotia (Schwartz et al. 2013). As of 2007, complete records are available for 26 sites since 1993 and for 30 sites since 1994. In 2003, monitoring was discontinued at 47 sites. All sites with number above 400 were started in 1996. In 2004, sites 224 and 270 were added to the monitoring program. As of 2012, total numbers of samples collected to date from the currently monitored 43 sites are: Abrams Creek (372); Cataloochee Creek (772); Cosby Creek (451); Little River (227); Oconaluftee River (458); Road Prong (827); and Hazel Creek (466). In 2012, 186 samples from the current 43 sites were collected and processed. These totals do not reflect data associated with samples from sites that are no longer sampled.
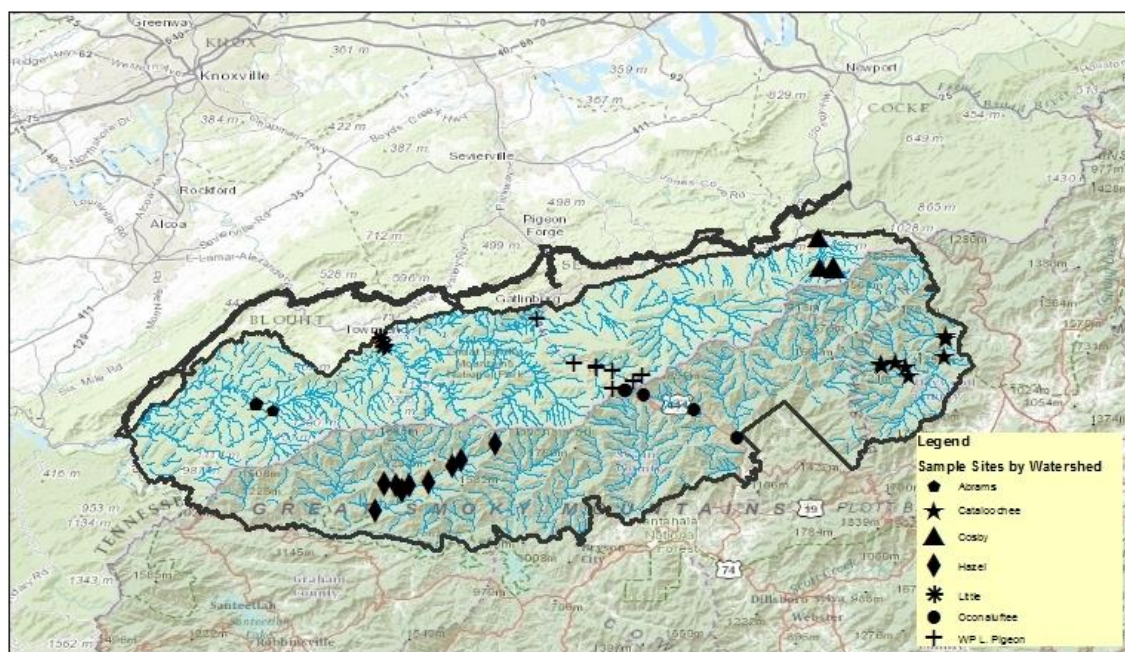
Figure 8. Currently sampled sites for the GRSM Park-wide stream survey water quality monitoring program. "WP L. Pigeon" includes Walker Prong, West Prong, and Road Prong as well as the West Prong of the Little Pigeon.

3.2 Study Activities and Methods

Abrams, Cataloochee, Cosby, Little River, Oconaluftee, and Road Prong drainage basins were sampled bimonthly (January, March, May, July, September and November). Hazel Creek drainage basin was sampled twice per year (April and November). Water samples from these sites were collected as grab samples with no air/headspace in labeled, clean 250-mL polypropylene bottles. Sample bottles are transported back to the UTK CEE laboratory chilled to 2°C - 6°C, until analyzed. All water samples were analyzed for pH, conductivity and alkalinity at lab temperature within 48 hours of collection, and for primary anions (chloride, nitrate, sulfate), base cations (sodium, potassium, magnesium, calcium), and ammonium species. Currently, sub-samples were filtered through 0.45 µm membrane filters and acid-preserved to pH < 2 (with ultra-pure spectroscopy grade nitric acid) prior to being analyzed by inductively-coupled plasma atomic emission spectroscopy (ICP-AES) within 2-6 months of collection. Various quality assurance (QA) samples and standards also were subjected to these same analytical protocols to demonstrate precision and accuracy of laboratory analyses. It should be noted that metal analysis by the ICP-AES method started in 2003. Trace metals (aluminum (Al), copper (Cu), iron (Fe), manganese (Mn), dissolved silicon/silica (Si) and zinc (Zn)) were not quantified prior to that time, and base cations [sodium (Na), potassium (K), magnesium (Mg) and calcium (Ca)] were determined by alternate analytical techniques.

Data generated from these laboratory analyses were organized by sample ID and site ID, and converted to concentrations in micro-equivalents per liter. The raw analytical data were subjected to a number of standard numerical calculations to evaluate internal consistency of laboratory analytical results, and to derive water quality metrics related to field conditions. Spatial and temporal trends, overall ion balance, and inter-parameter correlations were evaluated from the raw analytical data. Ultimately the final datasets were transferred to NPSTORET.

In addition to these sample-specific QA and data-analysis procedures (Section 5.0), trends in GRSM water quality were assessed using these analytical data. The data were segregated by drainage basin or by site location, and evaluated for correlations with other known environmental factors (such as, elevation, geology, season, or known pollutant source). Preliminary results of these data assessments were described in the following sections, organized by drainage basin.

3.3 Park-Wide Water Chemistry: Watershed Summary

The water chemistry dataset of the GRSM monitoring program was evaluated for trends and correlations. The high degree of variability observed when assessing the combined dataset among watersheds provided a general assessment of GRSM water quality trends (e.g., Robinson et al. 2008), but limited defining water quality trends per watershed-specific chemistry and other factors. In contrast to prior annual reports, this report's approach was to divide and reorganize the dataset into subsets based on a number of factors: drainage basin, individual sampling site, year or multi-year period, season and elevation. This approach helped explain the observed data variability among all sites, and exposed patterns and relationships within the GRSM data.

The first level of classification was by drainage basin. Water quality data for each drainage basin were compiled, and average values over the period of record were calculated for: conductivity (µS/cm), pH (standard units), acid-neutralizing capacity ANC (µeq/L), sum of major anions (µeq/L), sum of major cations (µeq/L), and total inorganic solutes (TIS; µeq/L). The results are shown in Table 4. The results were sorted by mean pH (lowest to highest) and discussed below.

Initially, data for all Abrams Creek sampling sites were summarized together. On closer inspection, stark differences in water chemistry among individual sites became evident. The Abrams Creek

sites were subdivided into Mill Creek sites (Sites 173 and 488) and Abrams Creek sites (Sites 174 and 489). These are designated as "ABR Mill Creek" and "ABR Main Stem" in Table 4. The differences in water chemistry are clear. For most parameters, the levels observed in Abrams Creek sites exceed those in the Mill Creek tributary sites, as well as all other drainage basins. The unique characteristics of the Abrams Creek drainage basin are discussed later in this Section. These drainage basin-specific differences justified evaluating the GRSM water chemistry data on a drainage basin basis and on an individual site basis.

The chemistry of stream acidification is essentially an acid titration of carbonate-based buffer capacity. As stream pH increases (becomes less acidified), the natural acid-neutralizing buffer capacity of adjacent soils should have increasing influence on the system. The internal consistency of the current Park-wide dataset is evident when the overall mean pH for each drainage basin is compared to its overall mean ANC (Figure 9). Over the period of record as would be expected per carbonate buffer system chemistry: water from drainage basins with overall lower pH have relatively lower buffer capacity (as ANC), and water from the two sites in the upper reach of Abrams Creek have higher pH and higher buffer capacity (as ANC).

Another factor influencing the stream water chemistry of the GRSM is exposure to atmospheric deposition of acid-forming pollutants. Elevation can be used as a surrogate measure for degree of exposure to atmospheric deposition. Overall mean pH of each sampling site (over the period of record) was compared to site elevation (in meters). The result as shown in Figure 10 is the expected inverse relationship between elevation and pH, modeled here as a quadratic function to emphasize the non-linear nature of environmental processes ($r^2 = 0.426$). After deposition, fate and transport is governed by soil biogeochemical processes. A portion of soil water is rapidly drained to stream by what is termed interflow, and a portion of the water enters groundwater flow. Lower elevation streams may be influenced by long-term pollutant transport via groundwater flow, where groundwater inputs occur and may also influence water quality.

Table 4. Data summary of selected water chemistry parameters for entire period of record, organized by drainage basins. Note: Abrams Creek drainage basin is divided into two subsets, Mill Creek sampling sites and Main Stem sampling sites.

Drainage Basin Name/Designation	Mean Conductivity μS/cm	Mean pH	Mean ANC μequiv/L	Mean Σ(anions) μequiv/L	Mean Σ(cations) μequiv/L	TIS μequiv/L
Road Prong	20.65	6.10	38.18	121.8	175.1	341.1
Cosby Creek	16.25	6.10	31.76	94.17	143.0	271.3
Oconaluftee	26.47	6.18	45.81	170.1	221.6	442.4
Hazel Creek	12.79	6.50	70.71	45.3	132.9	249.7
Cataloochee	14.39	6.60	79.07	48.3	143.6	271.6
ABR Mill Creek	18.46	6.60	114.39	56.3	184.6	356.0
Little River	19.57	6.74	113.67	65.3	565.1	744.5
ABR Main Stem	**90.89**	**7.40**	**883.96**	**83.4**	**999.0**	**1966**

Notes: ABR = Abrams Creek; ANC = acid-neutralizing capacity; TIS = total inorganic solutes
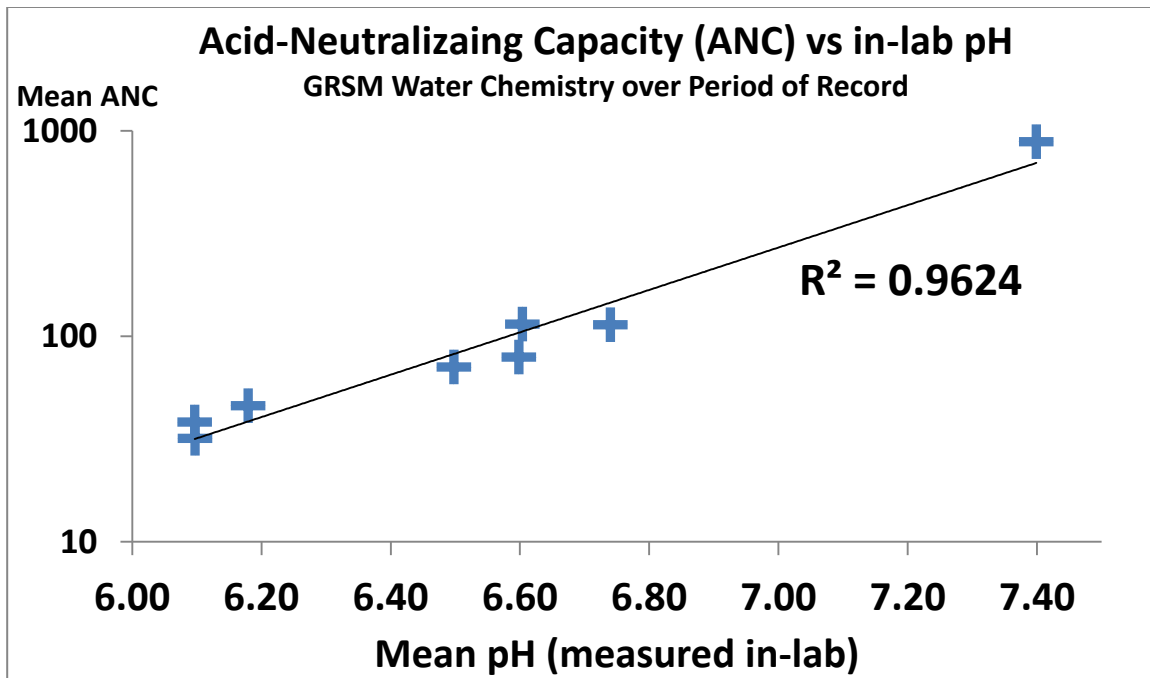
Figure 9. Correlation between Stream pH and Acid-Neutralizing Capacity (ANC). Data represent overall mean pH and ANC for individual drainage basins. ANC (ueq/L) is in log-scale.
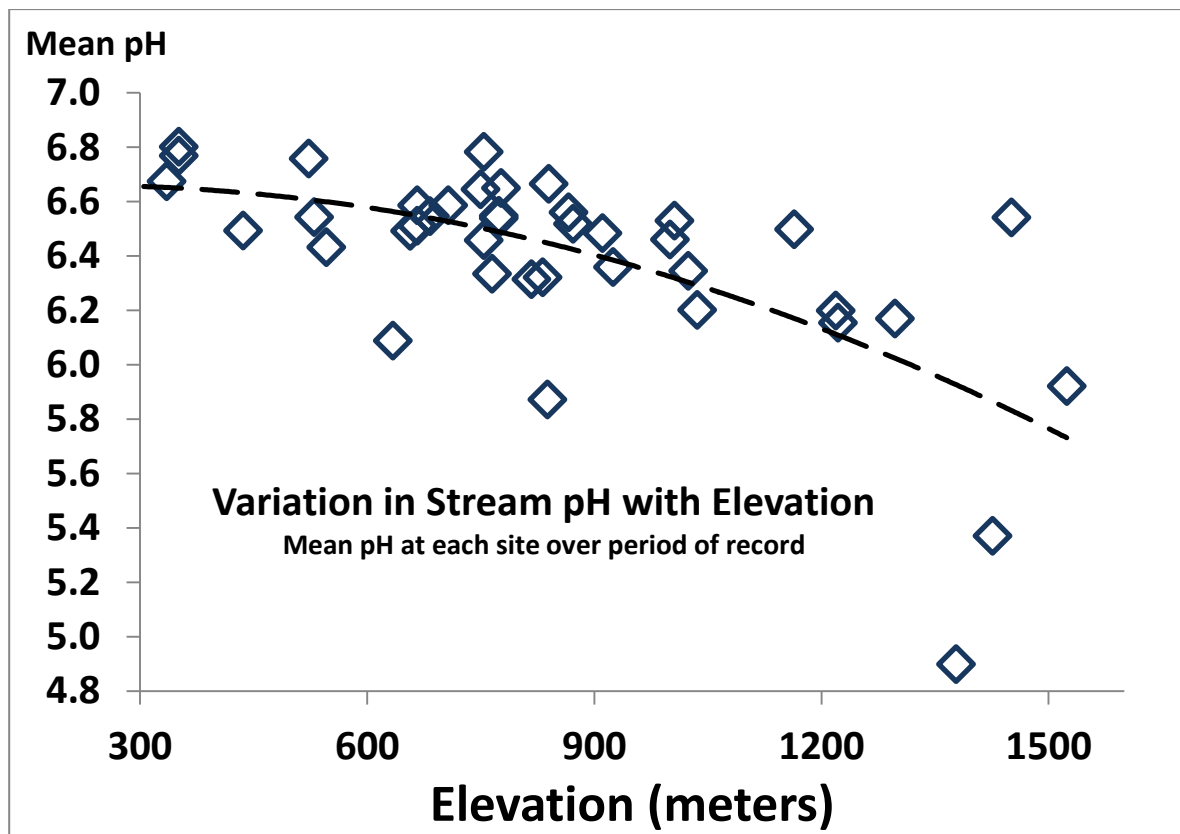
Figure 10. Stream pH at Monitored Sites (overall mean over period of record) versus Site Elevation (meters). The dashed line suggests a general correlation between mean pH and elevation.

3.3.1 Abrams Creek Water Chemistry

Data associated with four sampling locations (Sites 173, 174, 488 and 489) were available back to the beginning of the monitoring program (1993). As described earlier (Table 4), water chemistry of the four current Abrams Creek sampling sites were markedly different from all other monitored drainage basins. Closer evaluation of the Abrams Creek water chemistry data showed differences among individual sites within that drainage basin. Table 5 summarizes the mean values (over the period of record) of water chemistry parameters for the four sampling sites.

Table 5. Data summary of water chemistry (over the period of record) for Abrams Creek sampling sites.

Water Chemistry Parameter	Site 174	Site 489	Site 173	Site 488
Mean Conductivity (µS/cm)	96.3	84.3	23.8	12.4
Mean pH	7.37	7.44	6.76	6.43
Mean ANC (µeq/L)	938.2	817.9	174.0	47.3
Mean Σ(anions) (µeq/L)	84.7	81.9	55.8	56.8
Mean Σ(cations) (µeq/L)	1057.8	927.3	242.9	120.9
Mean TIS (µeq/L)	2080.7	1827.3	473.0	225.8

ANC = acid-neutralizing capacity; TIS = total inorganic solutes

Except for pH, magnitudes of water chemistry parameters at Site 489 (300 meters below Trailhead Bridge) were lower than those at Site 174 (below Cades Cove) but higher than those at the two Mill Creek sampling sites (173 and 488). The Mill Creek sites are not directly influenced by the Cove, The Loop, or the upper reach of Abrams Creek. Furthermore, the Mill Creek tributary system feeds into the Abrams Creek upstream of Site 489. Thus, the water chemistry at Site 489 (below Trailhead Bridge) reflects the flow-weighted dilution effect that Mill Creek has on Abrams Creek water chemistry (Table 5);

Of all currently monitored sites, Site 174 (below Cades Cove) was found to have the highest overall mean levels of conductivity, ANC, sum of cations and TIS (Table 5), potassium (15.7 µeq/L), magnesium (197.2 µeq/L), and calcium (789.5 µeq/L). Water chemistry from the upper reach of Abrams Creek was distinctly different than all other monitored locations in the GRSM, illustrating the strong influence of carbonaceous karst geology on stream chemistry at this location in the Park.

3.3.2 Cataloochee Creek Water Chemistry

Data for eight sampling locations (Sites 142, 143, 144, 147, 148, 149, 293 and 493) were available since 1993. Table 6 summarizes the mean values (over the period of record) of water chemistry parameters for the eight sampling sites. The sites are presented left-to-right in order from upstream to downstream.

Water chemistry was relatively consistent within the drainage basin; magnitudes of the selected water chemistry parameters do not vary drastically among the eight sampling sites. Based on water chemistry, the sites appeared to classify into three subgroups: Sites 142, 143 & 144; 493, 149 & 147; and 148 & 293. The most up-gradient sites in the Cataloochee Creek drainage basin had lower mean values for most water chemistry parameters, and concentrations increased with distance downstream. Water pH did not show any obvious spatial patterns, but varied by no more than ~0.3 pH units among all sampling locations.

Table 6. Data Summary of water chemistry (over the period of record) for Cataloochee Creek sampling sites.

Water Chemistry Parameter	Site 142	Site 143	Site 144	Site 493	Site 149	Site 147	Site 148	Site 293
Mean Conductivity (µS/cm)	11.6	11.8	12.4	14.0	14.6	14.8	17.1	17.7
Mean pH	6.53	6.46	6.48	6.56	6.65	6.64	6.78	6.66
Mean ANC (µeq/L)	58.3	56.9	58.3	79.2	80.3	83.5	117.9	95.1
Mean Σ(anions) (µeq/L)	42.4	45.1	47.2	44.5	47.7	47.3	43.9	62.5
Mean Σ(cations) (µeq/L)	116.7	116.3	120.3	134.8	146.3	150.3	180.9	174.2
Mean TIS (µeq/L)	218.1	219.1	226.7	259.3	274.1	281.6	343.1	332.4

ANC = acid-neutralizing capacity; TIS = total inorganic solutes

3.3.3 Cosby Creek Water Chemistry

Data for four sampling locations (sites 4, 114, 137 and 492) were available back to program inception (1993). Table 7 summarizes the mean values (over the period of record) of water chemistry parameters for the four sampling sites.

Sites 4 and 137 have similar water chemistry, and Sites 114 and 492 have similar chemistry. Each pair is located on a different tributary branch of the upper Cosby Creek drainage basin. The overall mean values suggest higher calcium-carbonate content in soils drained by the main branch of upper Cosby Creek (Sites 114 and 492), as compared to the sites located within the Rock Creek tributary to Cosby Creek (Sites 4 and 137). Water pH also showed some spatial differences, consistent with the hypothesis of different soil buffer content between the two tributary branches.

Table 7. Data Summary of water chemistry (over the period of record) for Cosby Creek sampling sites.

Water Chemistry Parameter	Site 4	Site 137	Site 114	Site 492
Mean Conductivity (µS/cm)	14.0	15.2	17.3	19.2
Mean pH	6.09	5.87	6.33	6.32
Mean ANC (µeq/L)	36.7	12.0	37.4	51.4
Mean Σ(anions) (µeq/L)	73.2	101.0	99.5	103.6
Mean Σ(cations) (µeq/L)	129.8	129.3	153.4	169.2
Mean TIS (µeq/L)	242.2	245.5	291.4	325.4

ANC = acid-neutralizing capacity; TIS = total inorganic solutes

3.3.4 Little River Water Chemistry

Data for three sampling locations (Sites 13, 23 and 24) were available since the program began in 1993. Table 8 summarizes the mean values (over the period of record) of water chemistry parameters for the three sites.

Table 8. Data Summary of water chemistry (over the period of record) for Little River sampling sites.

Water Chemistry Parameter	Site 13	Site 23	Site 24
Mean Conductivity (µS/cm)	18.0	16.7	21.8
Mean pH	6.67	6.77	6.80
Mean ANC (µeq/L)	99.6	79.8	135.3
Mean Σ(anions) (µeq/L)	63.6	69.9	66.0
Mean Σ(cations) (µeq/L)	180.5	160.0	220.8
Mean TIS (µeq/L)	344.4	310.1	422.4

ANC = acid-neutralizing capacity; TIS = total inorganic solutes

Identifying correlations or drawing conclusions about overall water chemistry (over the period of record) was difficult when comparing data from only three sites. Water chemistry was relatively consistent among the three sites, and was generally indicative of a non-impacted stream.

3.3.5 Oconaluftee River Water Chemistry

The dataset associated with five sampling locations (Sites 251, 252, 253, 268 and 270) included data back to 1993. Table 9 summarizes the mean values (over the period of record) of water chemistry parameters for the five current sampling sites. The sites were arranged left-to-right in Table 9 in the order they occur within the River, from upstream to downstream.

Water chemistry in this drainage basin showed some spatial trends. From Site 252 to Site 268, chemistry parameters decreased with distance downstream; pH increases reflecting decreasing acidity with distance downstream. Site 253, which is immediately up-gradient of Site 252, does not follow this pattern, and it appears similar to Site 251 water chemistry. The general trend in water chemistry is decreasing concentrations with distance downstream, suggesting a dilution effect by tributaries feeding the main stem. Thus, the predominance of water solutes in this drainage basin originates from the upstream headwaters most heavily exposed to acid deposition. Water from Site 252 had the highest aluminum (0.435 µeq/L) and manganese (0.418 µeq/L), second highest zinc (0.0485 µeq/L), third highest magnesium (122.5 µeq/L), and the fourth highest iron (0.045 µeq/L) and calcium (137.3 µeq/L).

Table 9. Data Summary of water chemistry (over the period of record) for Oconaluftee River sampling sites.

Water Chemistry Parameter	Site 253	Site 252	Site 251	Site 270	Site 268
Mean Conductivity (µS/cm)	29.3	44.4	25.2	14.3	12.9
Mean pH	6.15	5.37	6.54	6.51	6.44
Mean ANC (µeq/L)	24.7	12.5	84.2	63.3	47.4
Mean Σ(anions) (µeq/L)	208.3	340.5	128.2	61.0	61.0
Mean Σ(cations) (µeq/L)	251.9	325.6	225.2	138.2	116.5
Mean TIS (µeq/L)	486.6	697.2	438.9	263.2	225.8

ANC = acid-neutralizing capacity; TIS = total inorganic solutes

3.3.6 Road Prong Water Chemistry

Eight sampling locations within this drainage basin (Sites 30, 66, 71, 73, 74, 233, 234 and 237) have been monitored since 1993. Table 10 summarizes the mean values (over the period of record) of water chemistry parameters for the eight sampling sites. The sites were arranged left-to-right in Table 10 roughly in upstream to downstream order. Sites 237, 233, 74 and 73 are located in the

Walker Camp Prong watershed, and Sites 234 and 71 are located in Road Prong watershed. Downstream of the confluence of those two branches are Sites 66 and 30.

Water chemistry in this drainage basin shows a few spatial trends. The strongest trend in seen in water pH; it increases (that is, acidity decreases) with distance downstream. Corresponding to the acidity gradient is the ANC concentration, which goes from an overall average in the negative ANC range (Site 237) to larger values further downstream. Weaker trends in solute concentrations are seen with conductivity and TIS increasing with distance downstream. This is a more typical pattern for watersheds that accrue dissolved material as groundwater contributions increase. Thus, water solutes in this drainage basin do not come from only one location (e.g., the headwaters), but are dispersed throughout the drainage area.

Table 10. Data Summary of water chemistry (over the period of record) for Road Prong/Rt.6 sampling sites.

Water Chemistry Parameter	Site 237	Site 234	Site 233	Site 74	Site 73	Site 71	Site 66	Site 30
Mean Conductivity (µS/cm)	19.9	15.6	24.1	26.4	21.7	16.0	20.0	20.7
Mean pH	4.90	5.92	6.17	6.50	6.34	6.20	6.31	6.49
Mean ANC (µeq/L)	-11.5	18.9	35.5	79.4	50.9	30.9	40.5	61.9
Mean Σ(anions) (µeq/L)	124.1	98.2	154.8	141.3	128.5	95.8	117.8	111.6
Mean Σ(cations) (µeq/L)	112.5	130.1	206.4	237.2	196.0	144.4	178.8	192.2
Mean TIS (µeq/L)	257.8	250.2	399.9	459.2	376.8	272.8	338.4	366.6

ANC = acid-neutralizing capacity; TIS = total inorganic solutes

3.3.7 Hazel Creek Water Chemistry

Eleven locations (Sites 211, 224, 310, 311, 479, 480, 481, 482, 483, 484 and 485) were sampled as part of the current monitoring program. Data for most sites were available back to 1996; Sites 221, 310 and 311 have been sampled and analyzed since 1993. Table 11 summarizes the mean values (over the period of record) of select water chemistry parameters for the 11 sampling sites. The sites are arranged in Table 11 from left to right, in roughly an upstream-to-downstream order as they are located within this drainage basin.

Water chemistry was relatively consistent within the drainage basin; differences in magnitudes of the selected water chemistry parameters vary only slightly among the 11 sampling sites. There appear to be subgrouping of sites, based on water chemistry. Sites 221, 224 and 484 are situated within Hazel Creek from upstream to downstream. Most water chemistry parameters showed a consistent increase concentration with distance downstream, the exception being the acid anions. The other apparent subgrouping of sites consisted of Sites 482, 483 and 484. Their water chemistry was similar in concentration, reflecting their proximity to each other.

Site 481 is located in the same area, but its water chemistry (except for pH) was markedly different. It suggests that its water chemistry may be influenced by the Old Mine in that area. Interestingly, the overall mean concentrations (over the period of record) of aluminum (0.053 µeq/L), copper (0.075 µeq/L), manganese (0.084 µeq/L), zinc (0.156 µeq/L), and to a lesser degree iron (0.072 µeq/L), were the highest among the sampling sites in this drainage basin, and the mean concentrations of copper and zinc at Site 481 were the highest among all currently sampled sites (over the period of record). Site 481 is located in the tributary upstream of Sites 483 and 480, and the water chemistry at those sites reflects the influence of that tributary (Table 11).

Table 11. Data Summary of water chemistry (over the period of record) for Hazel Creek sampling sites.

Water Chemistry Parameter	Site 221	Site 224	Site 484	Site 485	Site 310	Site 311	Site 479	Site 481	Site 482	Site 483	Site 480
Mean Conduct. (µS/cm)	10.5	10.5	10.7	11.2	12.6	11.9	11.8	18.2	13.8	14.6	13.6
Mean pH	6.20	6.36	6.46	6.52	6.55	6.49	6.54	6.54	6.55	6.59	6.59
Mean ANC (µeq/L)	28.7	43.0	54.9	71.4	76.9	66.1	68.8	86.5	89.3	86.6	85.6
Mean Σ(anions) (µeq/L)	57.8	44.1	38.7	34.0	41.2	40.5	38.1	77.4	40.4	47.3	40.0
Mean Σ(cations) (µeq/L)	101.1	100.6	111.6	124.6	131.4	124.9	125.2	177.1	149.1	154.3	143.1
Mean TIS (µeq/L)	189.1	188.9	206.0	230.8	250.1	232.2	232.8	341.7	279.5	288.8	269.4

ANC = acid-neutralizing capacity; TIS = total inorganic solutes

3.4 Park-Wide Water Chemistry: Temporal Trends

Descriptive statistics (minimum, maximum, average of the median values across all Stream Survey sites, standard deviation, and coefficient of variation) of WQ parameters measured in 2012 at the 43 survey sites are summarized in Table 12. Also shown are percent differences between the 2012 results and the historical results from 1993-2011. This analysis examines all the sample sites collectively providing a general trend analysis for the park-wide data. A more detailed analysis of trends can be found in Schwartz et al. (2013) where trends varied by site elevation. Additional trends analyses will be conducted with the dataset examining watersheds separately, but that effort is beyond the scope of this annual report. General trends from the dataset are reported below.

In 2012, the mean pH of 6.499 increased 0.06 units from the historic mean (1993-2011) of 6.437 (Table 12). ANC increased 63.6% from a historic mean of 57.5 µeq/L to 94.1 µeq/L. To note, mean ANC is heavily influenced by measurements from Abrams Creek. Sulfate and chloride mean concentrations and base cation mean concentrations (sodium, potassium, magnesium, and calcium) all declined from the historic mean (1993-2011) to 2012. Mean nitrate concentration in 2012 did not show a major change with historic mean concentrations. In 2012, concentrations of copper, manganese and silicon decreased from their historical medians while iron, aluminum, and zinc increased. Mean dissolved aluminum increased 39.3% from the historic mean to 2012. It should be noted that apparently larger percent differences for dissolved metals as compared to those of other ions are an artifact of their very low concentrations in these samples; slight differences in low concentrations result in large calculated percentages.

3.5 Park-Wide Water Chemistry: Toxicological Thresholds

In Cai et al. (2013), a literature review of toxicological thresholds was completed, where pH, aluminum, and zinc were the primarily parameters of concern in the GRSM. Trout growth is impacted about 5.5 or less, and reduced abundance about 5.0 or less. Tennessee and North Carolina State Water Quality Standards required waters to be between 6.0 and 9.0. Of the 43 sites currently monitored, 20 sample exceedences were below pH 6.0 (N = 186; Table 6). The minimum pH reported was 4.73 (Table 6). Toxic thresholds for total dissolved aluminum and zinc were > 0.20 mg/L and > 0.219 mg/L, respectively. The number of sample exceedences for dissolved aluminum and zinc were 14 and 1, respectively. Most of the water quality exceedences occurred in the Cosby Creek, Oconaluftee River, and Road Prong watersheds (Table 5).

Table 12. Descriptive statistics of 2012 median water quality values for the 43 Park-wide stream survey sites. Chemistry units as shown per water quality parameter.

Water Quality Parameter	Minimum	Maximum	Mean	Standard Deviation	CV	Percent Difference *
Median pH	4.734	7.959	6.499	0.612	0.094	+0.97
Median ANC (µeq/L)	-18.285	1409.209	94.011	214.33	2.280	+63.59
Median Conductivity (µS/cm)	0.600	135.300	17.928	19.821	1.106	-11.60
Median Chloride (µeq/L)	0.000	28.799	10.830	6.652	0.614	-21.86
Median Nitrate (µeq/L)	0.000	65.207	19.423	17.031	0.877	+0.21
Median Sulfate (µeq/L)	0.000	317.633	42.217	44.791	1.061	-9.09
Median Sodium (µeq/L)	0.000	68.388	31.408	15.651	0.498	-18.91
Median Ammonium (µeq/L)	0.000	9.778	1.408	1.743	1.238	--
Median Potassium (µeq/L)	0.000	17.029	8.161	4.505	0.552	-23.92
Median Magnesium (µeq/L)	0.197	247.664	36.750	39.376	1.071	-11.97
Median Calcium (µeq/L)	0.000	1158.699	92.854	171.34	1.845	-5.59
Median Aluminum (ppm)	0.000	0.514	0.063	0.082	1.293	39.30
Median Copper (ppm)	-0.003	0.147	0.001	0.011	7.863	-17.14
Median Iron (ppm)	0.000	0.460	0.035	0.057	1.623	+91.51
Median Manganese (ppm)	0.000	0.295	0.007	0.032	4.741	-15.94
Median Silicon (ppm)	0.000	5.214	2.270	1.174	0.517	-17.89
Median Zinc (ppm)	0.000	0.264	0.013	0.026	2.004	+50.81

 * Percent Difference = (2012 average – 1993-2011 average)/(1993-2011 average) ×100%.

Table 13. Number of toxicological exceedences for pH, dissolved aluminum, and dissolved zinc among the total number of samples collected in 2012. N = 186.

Watershed	pH < 5.5	pH < 6.0	Al > 0.20 mg/L	Zn > 0.219 mg/L	Total Count
Cosby Creek	2	10	3	0	15
Little River	0	0	0	0	0
Road Prong	3	3	6	0	12
Oconaluftee River	5	6	4	0	15
Abrams Cr.	0	0	0	0	0
Cataloochee Creek	0	1	1	0	2
Hazel Cr.	0	0	0	1	1
Total Count	10	20	14	1	45

Note: an exceedence for pH < 5.5 is also counted in the exceedence number for pH < 6.0.

4.0 Watercress Branch Recovery Study

4.1 Introduction
On April 22, 2010 at about 11:00 AM, a concrete truck loaded with dry concrete mix rolled off of Cherokee Orchard Road (Mile Marker = 0.5) and came to rest on its side laying in Watercress Branch. The truck leaked a small amount (< 5 gallons) of diesel fuel and roughly 2 cubic yards of dry concrete mix onto the steep bank and surrounding vegetation, and into the stream (Ray Bell, HEPACO, Inc., *personal comm.*). The affected area was roughly 90 ft in diameter. Shortly after the accident, numerous GRSM staff evaluated the area from the truck rollover site downstream to the confluence with Leconte Creek. Numerous dead salamanders (> 50) and stoneflies (> 50) were found, and one severely impacted brook trout (150 mm in length) were found during this initial assessment. The affected area had a strong smell of diesel fuel and rainbow sheen on the water surface was observed on top of the water.

On Friday April 23, 2010 at 9 AM, Kulp and Nichols (GRSM Biologists) returned independently to the site to evaluate impacts in the rollover area. Kulp observed between 75-100 dead salamanders between the rollover site and the confluence of Watercress Branch and a small tributary, just upstream of Leconte Creek. Also observed were numerous dead small insects and aquatic worms.

4.2 Study Activities and Methods
Soon after the accident, water samples were collected above (n = 1) and below (n = 2) the spill site and analyzed for pH and alkalinity at the UTK-CEE lab. The two downgradient sampling locations are designated as Site 1 (located roughly 300 feet downstream of the spill site) and Site 2 (located roughly 800 feet downstream of the spill site, just upstream of the confluence with Leconte Creek). Nichols collected (d-net sampling) and preserved macroinvertebrates at locations above and below the spill site. A second set of water samples was collected at those same locations and analyzed for pH and alkalinity.

To evaluate long-term recovery of the site, water quality samples were collected quarterly to distinguish effects caused by the spill from effects related to potential (natural) seasonal variation from spill effects. For each sample period, water quality samples were collected above the spill area (control) and two locations downstream of the spill area (effected area). The control site was located roughly 230 feet upstream of the spill site.

Stream water samples were analyzed to distinguish differences between the control site and the sites possibly affected by the spill. The degree to which water quality deviated from control site conditions was used as an indicator of how well the site has recovered to pre-spill conditions. Water quality collection and analysis were done according to USGS protocols. Water samples were collected, chilled and transported to the UTK-CEE lab for analysis. Each sample was analyzed for conductivity, pH, alkalinity, phosphate, nitrate, sulfate, and common anions and cations. Water samples also were analyzed for metals (Al, Cu, Fe, Mn, Si and Zn) to evaluate potential leaching of metals from surrounding soils into the stream.

4.3 Water Quality Analysis – Spatial Trends
Initial samples had observable differences in water quality between an unimpacted upstream location (control) about 230 ft upstream of the rollover site, and two downstream locations: S1 (about 300 ft downstream of the site) and S2 (about 800 ft downstream of the site). Initial differences in pH (158%), conductivity (1,938%) and ANC or alkalinity (1,620%) persisted into the second day post-spill (Table 14). Water conductivity and alkalinity decreased substantially over 24

hours but not to pre-spill levels; stream pH remained high for at least 24 hours after the spill. Results of the later analyses are presented in Figure 11, which shows the mean values of five water quality parameters (pH, conductivity, ANC, total anions and total cations) in water samples from the upstream "Control Site" and the two downstream sample locations (S1 and S2). The error whiskers represent one standard deviation above and below the calculated mean.

Table 14. Water quality results from samples collected immediately after the concrete truck rollover event on Watercress Branch, April 22-23, 2010.

Location	Date	pH	Conductivity (µS/cm)	ANC (mg/L)
Control Site	April 22, 2010	6.93	15.8	132.1
Sample 1 (S1)	April 22, 2010	10.97	306	2,140.7
Sample 2 (S2)	April 22, 2010	10.74	227	1,769.3
Control Site	April 23, 2010	7.08	16.5	132.1
Sample 1 (S1)	April 23, 2010	10.12	99	901.1
Sample 2 (S2)	April 23, 2010	9.93	85	849.3

* D:\GRSM\2012 work files\Water-Cress\Road_Construction_GRSM (2013).xlsx
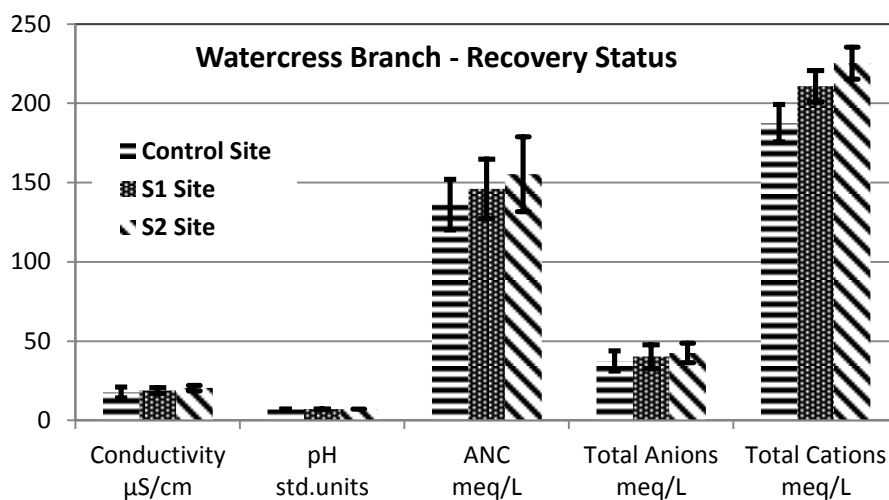
Figure 11. Watercress branch water quality indicators of stream recovery. Units: conductivity (µS/cm); pH standard units; ANC, total anions, and total cations (meq/L). Error bars represent ± one standard deviation.

To test whether measured differences were statistically significant, pair-wise t-tests were run at an α of 0.05, and shown in the table below. Pairings consisted of: Control – S1; Control – S2; S1 – S2 .

Water Quality Parameter	p-values for t-test pairings		
	Control / S1	Control / S2	S1 / S2
Conductivity	0.42712	0.14830	0.18064
pH	0.17829	**0.09549**	0.61905
ANC	0.30107	0.20936	0.80397
Total Anions	0.53048	0.26988	0.55256
Total Cations	0.00647	0.00126	0.03246

Based on this statistical test, the magnitudes of most water quality parameters over a one year period (November 2011 to November 2012) were not statistically different among sampled locations along the Watercress Branch. Differences in total cations concentrations in the downstream direction appear to be larger than those attributable to sampling and measurement variation. Also, differences in pH between the Control Site and the furthest downstream site (S2) approached significance (0.095), but were greater than the chosen significance level. The data indicate that the reach of Watercress Branch has recovered to pre-spill conditions.

4.4 Water Quality Analysis – Temporal Trends

The same water quality data from the three Watercress Branch sites were plotted against collection date to evaluate potential time-trends. Figure 12 shows the time-series data for pH and conductivity (µS/cm); Figure 13 shows the time-series data (in meq/L) for total nutrient cations (ammonium, sodium, potassium, magnesium and calcium), ANC, and total anions (chloride, nitrate and sulfate). In each case, a linear regression line is plotted with the measured values. The slopes of the regression lines provide qualitative information as to the general time-trend of the water quality parameters; a flat regression line (slope = 0) could indicate an equilibrium stream condition.

Figure 12 shows that the variation in stream pH over time was negligible; the slopes of the lines are nearly zero. Over the 12 month period represented by these data, stream water pH at each site was relatively constant. Conductivity shows an obvious increasing trend from about 15 to 23 µS/cm;
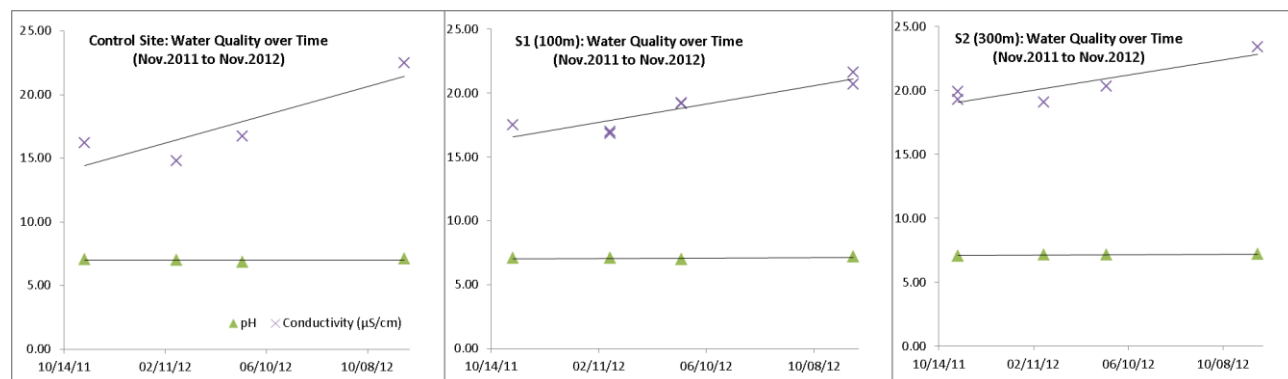
Figure 12. Temporal trends in pH and conductivity in Watercress Branch (November 2011 through November 2012).
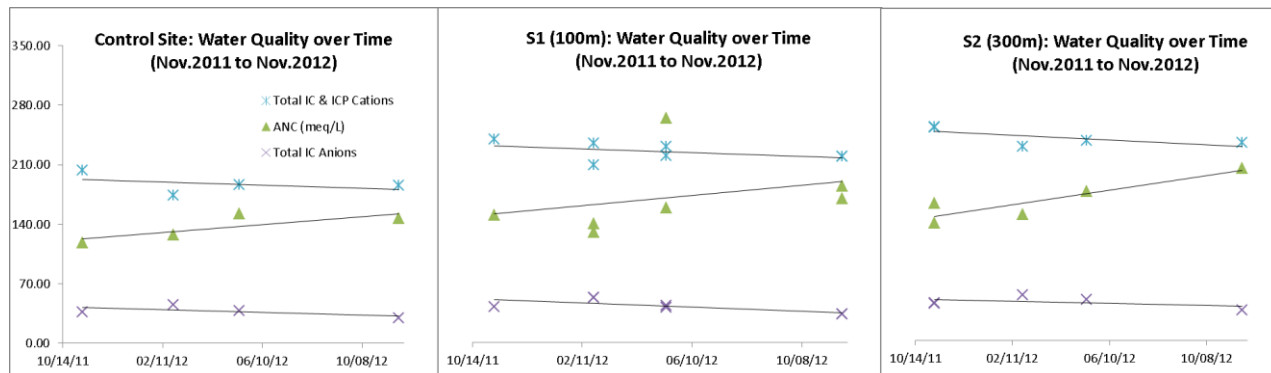
Figure 13. Temporal trends in anions, cations, and acid-neutralizing capacity (ANC) in Watercress Branch (November 2011 through November 2012).

however, relative to samples collected immediately after the spill event and one year after the spill (Table 14), the variation in stream water conductivity was marginal.

Figure 13 shows that the variation in total cations and anions concentrations is almost negligible; there is a very slight decreasing trend in concentrations. In the case of ANC, the data showed an obvious increasing trend; however, relative to samples collected immediately after the spill event and one year after the spill, variation in stream water ANC was marginal.

Based on these data, the surface water quality in this reach of Watercress Branch has equilibrated to pre-spill conditions. The trends over time at all three sites, including the "unimpacted" upstream control site, are qualitatively and quantitatively equivalent. The observed trends are unrelated to the spill.

5.0 Laboratory Analysis: Quality Assurance\Quality Control

Analytical procedures used to chemically analyze water samples for pH, ANC, conductivity, ions, and dissolved metals were based upon approved standard methods (Appendix A). WQ results for all samples are reported and archived in the NPSTORET database, however data quality is reported here. In 2012, 404 water samples were analyzed: (i) NDW precipitation at OS and TF, soil lysimeter, and SW/NE stream water samples (N = 143); (ii) Park-wide Stream WQ Survey grab samples, including Hazel Creek (N = 246); and (iii) Watercress Branch stream recovery study samples (N = 15).

Water samples collected in the field were transported to UTK-CEE lab and within 48 hours samples were analyzed for pH, ANC, and conductivity. Park-wide samples collected by volunteers from Trout Unlimited were taken to the GRSM WQ field refrigerator for storage; the 48-hour hold time requirement may not have been met by these samples. Analyses for pH, conductivity and gran ANC were conducted at room temperature to standardize results among many samples collected from different locations, times, and temperatures. After completing these analyses, water samples were stored (refrigerated) for remaining analyses (i.e., ions and dissolved metals). UTK-CEE analytical instruments and procedures were optimized for low concentrations of dissolved constituents. Thus, dilution was only necessary for constituents present in samples at high concentrations. Precision and bias of all WQ analyses and data was inferred based on a number of laboratory QA\QC procedures: blanks (at least two per sample batch), split sample replicates (every 20 samples), "known addition" spikes (every 20 samples), and certified check standards (USGS standard solutions; one for every 10 samples). The results of those QA\QC procedures are presented in the following sections.

5.1 Ion Chromatography Quality Assurance\Quality Control

Three anions (chloride, nitrate and sulfate) and one cation (ammonium; NH_4^+) were analyzed on the Dionex™ ion chromatograph (IC). Standard solutions for the IC analysis were created from high-grade reagents and deionized (DI) water. DI water was tested for conductivity, and accepted conductivities were less than 1.0 micro-Siemens per centimeter (μS/cm). In addition, standard curves produced by the instrument were checked to insure a linearity of $R^2 > 0.9999$. Analytical detection limits on the IC, QA\QC results for blanks, replicate precision, and spike recovery efficiency are reported in Table 15, and the results of analysis of prior years' USGS certified quality control check (QCC) samples are reported in Table 16. Analytical results for current year's USGS certified QCC sample are presented in Section 5.4.

QA\QC results indicated good data quality for IC analyses in 2012. Constituent concentrations in sample blanks were near or below detention limits. Precision of replicate analyses for the three anions were excellent ($\leq 1\%$); for ammonium, it was 9%. Replicating ammonium concentrations at low levels is a common analytical challenge, given the sensitivity of the ammonium/ammonia equilibrium to pH. The recovery efficiency of chloride and ammonium were very good (100.2% and 99.6%, respectively; outliers were excluded from the calculation). Recovery efficiency of nitrate and sulfate were > 100%.

Replicate precision results for blind-Sample analysis (using past-years' USGS certified QCC samples) showed generally excellent repeatability. Percent differences for ammonium ranged widely (0.15%, 2.9%, -16.2 and 52.3%) and sulfate (16.5% and 24.9%). Repeatability of

chloride and nitrate were excellent, all percent differences were less than 2.8%. Given that the replicate precision was excellent for chloride, nitrate and sulfate in field-collected samples (Table 15), the relatively large differences noted for ammonium and sulfate in the old USGS QCC samples could indicate deterioration of those aged samples. We will order replacement QCC samples in the future.

Table 15. Ion chromatograph instrument and procedure QA/QC (anions and cations).

QA\QC Procedure	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+
Detection limits (DL, mg/L)	0.010 *	0.026 *	0.099 *	0.007
Concentrations in water blanks, mg/L (# of samples)	0.014 (31)	0.003 (31)	0.013 (31)	0.007 (35)
Replicate precision, absolute %-difference (# of samples)	1.01 (42)*	0.86% (39)*	1.02% (40)*	9.11% (28)*
Efficiency of spike recovery, % (# of samples)	100.2% (19)*	129.0% (19)	125.1% (19)*	99.6% (22)*

* Median can be used for non-symmetric, skewed sample-data distributions

Table 16. Ion chromatograph blind-sample accuracy QA/QC (anions and cations).

Sample (Year)*	Constituent	Reported mg/L	Actual (USGS)	% difference
N-101 (2009)	NH_4^+ (as N)	0.361 (N = 64)	0.360	0.15%
N-103 (2009)	NH_4^+ (as N)	0.329 (N = 76)	0.320	2.9%
	NO_3^- (as N)	0.274 (N = 3)	0.270	1.35 %
N-107 (2010)	NH_4^+ (as N)	0.186 (N = 24)	0.193	-16.2%
	NO_3^- (as N)	0.134 (N = 36)	0.135	-0.97%
N-111 (2011)	NH_4^+ (as N)	0.134 (N = 43)	0.280	-52.3%
	NO_3^- (as N)	0.303 (N = 16)	0.312	-2.76%
P-53 (2009)	Cl^-	1.05 (N = 17)	1.05	0.07 %
	SO_4^{2-}	0.349 (N = 17)	0.418	-16.5%
P-57 (2011)	Cl^-	2.23 (N = 78)	2.24	-0.39%
	SO_4^{2-}	0.150 (N = 78)	0.200	-24.9%

* Samples consist of past-years' USGS Round-Robin "blind" sample. Current year's results are presented later in this report. The UTK-CEE Water Quality laboratory is designated as "lab #228" in the list of participating labs.

5.2 Inductively Coupled Plasma-Atomic Emission Spectrometry QA/QC

Major cations (sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), and calcium (Ca^{2+})) and six trace metals (aluminum (Al), copper (Cu), iron (Fe), manganese (Mn), silicon (Si), and zinc (Zn)) were analyzed on the Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES). To demonstrate the quality of the data, several QA/QC procedures were performed during metals analyses of the current year water samples. Standards were prepared using certified ICP reagents and ultra-pure DI water. Standard curves produced by the instrument were checked for linearity ($R^2 > 0.99$) prior to sample introduction. The QCC samples were also prepared from the certified reagents and DI, and run every ten samples to monitor accuracy during each batch run. Analytical results for the QCC samples are presented in Table 17. As indicated, all analytes were detected with high accuracy: the coefficient of variation for all elements was < 4% (except magnesium at 4.7%).

Table 17. ICP-AES known-sample accuracy (quality control check standard).

Element	Mean (ppm)	Actual (ppm)	% Error *	CV **
Aluminum	0.4971	0.5000	0.58 %	3.60 %
Calcium	1.0222	1.0000	2.22 %	3.65 %
Copper	0.5001	0.5000	0.01 %	2.62 %
Iron	0.5044	0.5000	0.88 %	2.99 %
Potassium	0.9346	1.0000	6.54 %	2.49 %
Magnesium	0.9929	1.0000	0.71 %	4.70 %
Manganese	0.5038	0.5000	0.77 %	2.14 %
Sodium	0.4746	0.5000	5.07 %	3.77 %
Silicon	1.0064	1.0000	0.64 %	3.06 %
Zinc	0.4956	0.5000	0.87 %	3.46 %

* Error (%) = Absolute value of difference (mean – target) divided by target value, times 100.
** Coefficient of Variation (CV; %) = standard deviation divided by mean, times 100.
Number of independent measurements: N = 59

Quality assurance samples of trace metal solutions from USGS were analyzed to verify low concentration accuracy. This sample was included in each analysis-set at a rate of once per 10 to 12 field samples. Most probable values (concentrations) in the certified USGS QC sample (found at *http://bqs.usgs.gov/srs/*) were compared to the laboratory ICP-AES results (Table 18). Except for aluminum, copper and potassium, the coefficient of variation for the elements was < 10%, and all relative errors were < 3.8% (except potassium). It should be noted that the copper concentration in USGS quality assurance sample T-183 was near the detection limit of UTK-CEE's instrument; therefore, slight deviations from actual concentration yield large coefficient of variations.

Field and reagent blanks were analyzed to check for potential external metal contamination. Results for water blanks (DI water) are presented in Table 19. Results were in the very low parts per billion, indicating no detectable source of metal contamination at the UTK-CEE lab.

Table 18. ICP-AES blind-sample accuracy (trace metals using T-183 USGS reference sample)

Element	Mean Measured (ppm)	Actual (USGS)	% Error *	CV **
Aluminum	0.1255 (N = 51)	0.127	1.17 %	23.0 %
Calcium	11.53 (N = 52)	11.60	0.60 %	5.22 %
Copper	0.00374 (N = 52)	0.0036	3.77 %	24.5 %
Iron	0.2052 (N = 52)	0.206	0.36 %	5.11 %
Potassium	2.791 (N = 51)	2.57	8.62 %	5.02 %
Magnesium	7.749 (N = 51)	7.89	1.79 %	11.3 %
Manganese	0.0491 (N = 52)	0.0492	0.27 %	4.95 %
Sodium	13.14 (N = 51)	12.70	3.43 %	4.40 %
Silicon	3.786 (N = 52)	3.87	2.17 %	5.21 %
Zinc	0.0858 (N = 52)	0.0864	0.74 %	7.68 %

* Error (%) = Absolute value of difference (mean – actual) divided by actual value, multiplied by 100.
Rounding error can explain minor apparent discrepancies in totals.
** Coefficient of Variation (CV; %) = standard deviation divided by mean value, multiplied by 100.

Table 19. ICP-AES blank (deionized water) sample results

Element	Mean Value (ppm)
Aluminum	0.0102
Calcium	< 0
Copper	< 0.0001
Iron	0.0008
Potassium	< 0
Magnesium	0.0005
Manganese	0.0003
Sodium	0.0028
Silicon	0.0014
Zinc	0.0007

Number of independent measurements: N = 28

Additional quality checks were performed by analyzing split samples (true replicates) and spike-addition samples (recovery check). Randomly selected samples were prepared twice and included in each analysis-set at a rate of one per 20 field samples. Replicate analysis precision (as absolute % difference), spike recovery (% of mass added), and current ICP-AES detection limits are shown in Table 20. Note that results below the instrument detection limits (BDL) were excluded from the calculations. Also, note that low concentrations near the instrument detection

Table 20. ICP-AES instrument and procedure QA/QC (trace metals)

Element	Average Absolute % Difference *	N	Average % Recovery **	N	Current Detection Limits (mg/L)
Aluminum	43.2 %	15	102.1 %	18	0.021
Calcium	13.8 %	17	117.0 %	18	0.050
Copper	BDL	0	103.2 %	18	0.012
Iron	55.5 %	8	102.6 %	18	0.012
Potassium	1.78 %	16	103.8 %	18	0.165
Magnesium	21.6 %	20	109.7 %	18	0.001
Manganese	57.6 %	6	103.3 %	18	0.002
Sodium	19.0 %	17	126.7 %	18	0.041
Silicon	7.80 %	16	134.8 %	18	0.019
Zinc	30.8 %	11	103.5 %	18	0.008

* Difference (%) = absolute value of replicate results difference / replicate results average, multiplied by 100.

** Recovery (%) = measured concentration divided by the actual concentration, multiplied by 100.

limit can cause large percent errors for small variations in concentration. Sample spikes were also prepared and analyzed by ICP-AES. Recovery efficiencies ranged between 102% and 110%, except for calcium, sodium and silicon.

5.3 Ion Charge Balance Check

Quality assurance checks include computing relative ion-charge balance for all water samples collected in the field. The ion balance is calculated by summing the concentrations of all anions, cations, and dissolved metals within each sample. Ideally, the ion balance should be zero ("balanced"); that is, all charged ionic species are accounted for and are perfectly charge-matched. Deviations from zero could have several causes, such as the presence of unmeasured unaccounted dissolved ionic species in the sample (i.e., organic acids), differences in assumed dissolved metal ion charge, and poor analytical accuracy of measured ionic species. Ion-charge balance deviations can be either positive (excess cation charge) or negative (excess anion charge). Given that exhaustive analysis of water samples is impractical, some ion balance deviation is tolerable. USEPA guidelines suggest that a relative ion-charge balance within ±15% of zero is considered good recovery of all dissolved ionic species. Ion balances for the NE and SW streamlets, OS, and TF are summarized in Table 21.

Samples collected from the NE stream had ion balances deviations within the suggested tolerance range in 19 out of 20 samples. The annual average ion balance deviation for NE stream samples collected in 2012 was -4.7, and monthly ion balance deviations were all within the acceptable tolerance range. Only October had a slight positive deviation from charge balance. Samples collected from the SW stream had ion balances deviations within the suggested tolerance range in 19 out of 19 samples. The annual average ion balance deviation for SW stream samples collected in 2012 was -4.5%, and monthly ion balance deviations were all

Table 21. Ion Balance Calculations for Noland Divide Watershed (NE and SE streams, OS, and TF)

Ion balance deviation	NE Stream	SW Stream	OS	TF
Annual Average	-4.7%	-4.5%	-23.0%	-15.8%

within the acceptable tolerance range. Only December had a positive deviation from charge balance.

The annual average ion balance deviation for OS samples collected in 2012 was -23.0%; however monthly ion balance deviations were within the acceptable tolerance range in February, March, May and November. The OS samples are subject to alkalinity shifts because collected water can remain in the collector for up to 30 days. Because of this result for 2012, it is suggested we sample on a biweekly basis instead of a monthly frequency. Other years have not deviated to this percentage. The annual average ion balance deviation for TF samples collected in 2012 was -15.8%, and monthly ion balance deviations were within the acceptable tolerance range in March, May, and September through November.

5.4 USGS Round Robin Results

The UTK-CEE Water Quality Lab participates in an analytical evaluation program operated by the USGS. This program is not a laboratory certification program; however, participation is mandatory for laboratories that generate environmental data for USGS-sponsored projects and studies. One or more certified water samples are provided to UTK-CEE, and the samples analyzed by standard procedures. Later, USGS provides a table with most probable values (MPV) ("actual concentrations" in the certified samples), statistical Z-values (relative to other participating laboratories) and our laboratory's analytical precision (as percent difference from MPV) for constituents in the certified sample. Those metrics for all constituents in UTK-CEE's 2012 certified USGS sample are summarized in Table 22.

Results indicate good accuracy of analytical procedures (both IC and ICP-AES). The average relative differences between concentrations measured by the UTK-CEE Water Quality laboratory and the certified MPV concentrations are generally less than 7% for most constituents, and they range between 12% and 24% for ammonium, aluminum, iron, and sulfate. The extreme result for copper is a function of instrument detection limits and the fact that at low concentrations, small differences in measured concentrations result in large calculated percent differences.

Table 22. USGS Round-Robin laboratory study results (Fall 2012).

Sample	Analyte	UT-results	MPV [1]	Z-value	% difference
N-115 (Nutrients by IC)	NH_4^+ as N	0.20	0.230	-2.00	-13.04
	NO_3^- as N	0.23	0.229	0.11	0.44
T-211 (Trace Metals by ICP-AES)	Al	0.018	0.0145	2.82	24.14%
	Ca^{2+}	23.8	24.6	-0.77	-3.25%
	Cu	0.009	0.00124	49.74	625.8%
	Fe	0.061	0.0544	1.58	12.13%
	Mg^{2+}	5.16	5.21	-0.29	-0.96%
	Mn	0.045	0.0455	-0.25	-1.10%
	K^+	0.93	0.979	-0.86	-5.01%
	SiO_2^-	6.28	6.50	-0.65	-3.38%
	Na^+	9.80	9.78	-0.04	0.20%
	Zn	0.382	0.404	-0.88	-5.45%
P-59 Precipitation Sample (by IC and ICP-AES)	Ca^{2+}	0.495	0.490	0.33	1.02
	Cl^-	4.26	4.29	-0.23	-0.70
	Mg^{2+}	0.418	0.434	-0.67	-3.69
	pH	4.40	4.27	0.90	3.04
	K^+	0.224	0.210	0.67	6.67
	Na^+	0.168	0.171	-0.18	-1.75
	Conductivity	35.47	36.9	-0.51	-3.88
	SO_4^{2-}	0.45	0.512	-0.43	-12.11

All concentration data are in mg/L, pH in standard units, and conductivity in µS/cm.
 Most Probable Value; [2] Below instrument's detection limit.

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Appendix A: Analytical Procedures for Chemistry Analysis Performed at the University of Tennessee –Knoxville.

Analysis	Procedure	Equipment	Method References
pH	Potentiometric	PC-Titration Plus	EPA Method 150.1
Conductance	Potentiometric	PC-Titration Plus	EPA Method 120.1
Acid Neutralizing Capacity (ANC)	Automated Titration	PC-Titration Plus	Automated Gran Titration for low ionic strength waters, as in Hillman et al. 1986
Anions (NO_3^-, Cl^-, SO_4^{2-})	Ion Chromatography	Dionex Ion Chromatograph	Standard Methods 4110
Monovalent Cations (NH_4^+)	Ion Chromatography	Dionex Ion Chromatograph	Manufacturers Protocols
Earth and Trace Metals (Na^+, K+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Al^{3+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, & Si)	Inductively Coupled Plasma Spectrometer	Thermo-Electron Iris Intrepid II	Standard Methods 3120B EPA Method 6010B EPA Method 3005A

Standard Methods, AWWA (1995).

Appendix B: Site Locations for the Park-wide Stream Water Quality Program.

Site ID	Site Description	Latitude	Longitude	Elevation (m)	Stream Order	Stream System	Survey years (start - end year)
4	Lower Rock Creek	35.7613	-83.2104	634	2	Cosby Creek	1993-
13	Little River at boundary	35.6676	-83.7145	335	5	East Little River	1993-
24	Lower West Prong Little River	35.6568	-83.7102	351	4	West Little River	1993-
30	West Prong Little Pigeon at Headquarters	35.6882	-83.5367	436	4	West Prong Little Pigeon	1993-
66	West Prong Little Pigeon at Chimneys Picnic Area	35.6372	-83.4948	817	4	West Prong Little Pigeon	1993-
71	Road Prong above barrier cascade	35.6344	-83.4703	1036	3	West Prong Little Pigeon	1993-
73	Walker Camp Prong above Road Prong	35.6348	-83.4693	1024	3	West Prong Little Pigeon	1993-
74	Walker Camp Prong above Alum Cave Creek	35.6291	-83.451	1164	2	West Prong Little Pigeon	1993-
114	Cosby Creek at log bridge	35.7486	-83.2007	765	3	Cosby Creek	1993-
137	Upper Rock Creek (Cosby Creek)	35.7462	-83.2163	838	2	Cosby Creek	1993-
138	Inadu Creek (Cosby Creek)	35.7425	-83.227	1058	2	Cosby Creek	1993-
142	Beech Creek above Lost Bottom Creek	35.6356	-83.1454	1006	3	Cataloochee	1994-
143	Lost Bottom Creek (Cataloochee Creek)	35.6363	-83.1448	1000	2	Cataloochee	1994-
144	Palmer Creek above Pretty Hollow Cr	35.639	-83.1308	911	3	Cataloochee	1993-
147	Lower Cataloochee Creek	35.6669	-83.0728	750	4	Cataloochee	1993-
148	Lower Little Cataloochee Creek	35.6691	-83.0728	754	4	Cataloochee	1993-
149	Middle Cataloochee Creek at bridge	35.6463	-83.0755	777	4	Cataloochee	1993-
173	Mill Creek above Abrams Creek	35.591	-83.8536	523	4	Abrams Creek	1993-
174	Abrams Creek below Cades Cove	35.5919	-83.8531	523	4	Abrams Creek	1993-
221	Hazel Creek above cascades	35.5463	-83.5828	1219	2	Hazel Creek	1993-
233	Walker Camp Prong above Alum Cave	35.6183	-83.4272	1297	2	West Prong Little Pigeon	1993-
234	Upper Road Prong	35.6098	-83.4504	1524	1	West Prong Little Pigeon	1993-

Site ID	Site Description	Latitude	Longitude	Elevation (m)	Stream Order	Stream System	Survey years (start - end year)
237	Walker Camp Prong at last bridge	35.6241	-83.4169	1378	2	West Prong Little Pigeon	1993-
251	Beech Flats above US 441 loop	35.6023	-83.4153	1222	2	Oconaluftee	1993-
252	Beech Flats below roadcut	35.6067	-83.4339	1426	1	Oconaluftee	1993-
253	Beech Flats above roadcut	35.6068	-83.4351	1451	1	Oconaluftee	1994-
268	Oconaluftee River below Smokemont	35.5529	-83.3094	666	5	Oconaluftee	1994-
293	Rough Fork at Caldwell House	35.6244	-83.1139	840	3	Cataloochee	1993-
310	Bone Valley Creek (Hazel Creek)	35.4999	-83.6801	683	3	Hazel	1993-
311	Hazel Creek below Haw Gap Creek	35.4938	-83.6885	657	4	Hazel	1993-
479	Hazel Creek at Campsite 86	35.4723	-83.7193	530	4	Hazel	1996-
480	Haw Gap Creek near Campsite 84	35.4947	-83.6887	666	3	Hazel	1996-
481	Little Fork above Sugar Fork Trail	35.5026	-83.7084	774	1	Hazel	1996-
482	Sugar Fork above Little Fork	35.5024	-83.7086	774	2	Hazel	1996-
483	Sugar Fork above Haw Gap Creek	35.4995	-83.6949	707	2	Hazel	1996-
484	Hazel Creek at Cold Spring Gap Trail	35.5033	-83.6593	754	4	Hazel	1996-
485	Walker Creek above Hazel Creek Trail	35.5225	-83.6310	872	2	Hazel	1996-
488	Mill Creek at Pumphouse on Forge Creek Road	35.5835	-83.8345	546	3	Abrams	1996-
489	Abrams Creek 300 m below trailhead bridge	35.5914	-83.854	521	5	Abrams	1996-
492	Camel Hump Creek off Low Gap Trail	35.7446	-83.1988	832	1	Cosby	1996-
493	Palmer Creek at Davidson Branch Trail	35.6346	-83.1194	866	4	Cataloochee	1996-